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LABORATORY AND
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OF THE SEMI-VOST METHOD
VOLUME II: APPENDICES

by

J. Bursey, M. Hartman, J. Homolya,
R. McAllister, J. McGaughey, and D. Wagoner
Radian Corporation
3200 East Chapel Hill Road/Nelson Highway
Post Office Box 13000
Research Triangle Park, North Carolina 27709

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Project Officer

John Margeson
Quality Assurance Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27709

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

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16. ABSTRACT

An initial laboratory and field evaluation study has been completed which assessed the performance of the Semi-Volatile Organic Sampling Train Method (Semi-VOST) for measuring concentrations of principal organic hazardous constituents (POHCs) with boiling points greater than 100°C that are emitted from hazardous waste incinerators. A draft formulation of the methodology was tested through an experimental laboratory program to evaluate method performance characteristics. The program consisted of: (1) determination of minimum compound detection limits; (2) simulation of a flue gas stream to determine the impacts of water vapor, SO_2, NO_x, and HCl on sampling; and (3) determination of precision and bias for the sample preparation and analytical elements of the method. Results of the simulation study are reported for 12 test compounds (POHCs) representing a range of physical and chemical properties which could affect sample train collection and recovery performance. Three of the test compounds were selected for further investigation to evaluate method precision and bias under field conditions through the use of four simultaneously-operating Semi-VOST trains. Project results are presetned in Volume I along with recommendations on elements of the method requiring further research. Volume II includes appendices giving detailed descriptions of the method formulation, laboratory, and field studies along with quality assurance data.

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ABSTRACT

An initial laboratory and field evaluation study has been completed which assessed the performance of the Semi-Volatile Organic Sampling Train Method (Semi-VOST) for measuring concentrations of principal organic hazardous constituents (POHCs) with boiling points greater than 100°C that are emitted from hazardous waste incinerators. A draft formulation of the methodology was tested through an experimental laboratory program to evaluate method performance characteristics. The program consisted of: (1) determination of minimum compound detection limits; (2) simulation of a flue gas stream to determine the impacts of water vapor, SO_2, NO_x, and HCl on sampling; and (3) determination of precision and bias for the sample preparation and analytical elements of the method. Results of the simulation study are reported for 12 test compounds (POHCs) representing a range of physical and chemical properties which could affect sample train collection and recovery performance. Three of the test compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) were selected for further investigation to evaluate method precision and bias under field conditions through the use of four simultaneously-operating Semi-VOST trains. Cylinder gas standards of each compound were blended and dynamically spiked into paired sample trains for determining method bias. Estimates of bias are presented for toluene and 1,1,2,2-tetrachloroethane. Method precision for chlorobenzene is calculated from unspiked sample train results which also included distributive volume experiments to determine sample train breakthrough of POHCs. Project results are presented in Volume I along with recommendations on elements of the method requiring further research. Volume II includes appendices giving detailed descriptions of the method formulation, laboratory, and field studies along with quality assurance data.

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APPENDIX A

SAMPLING AND ANALYSIS PROCEDURES FOR THE DETERMINATION OF SEMI-VOLATILE COMPOUNDS FROM COMBUSTION SOURCES

INTRODUCTION

Appendix A is the draft of the Semi-VOST sampling and analysis method. With the exception of typographical errors and editorial comments, all changes and additions to the original draft method are listed below with the corresponding section number in which the changes or additions occur.

Section 1.3 - Previously listed as "to be determined," now included.

Section 1.4 - Previously listed as "to be determined," now included.

Section 1.5 - Previously listed as "to be determined," now included.

Section 2.1.5 - Teflon® or equivalent material is recommended as gasket material.

Sections 2.1.7 & 2.1.8 - Clarification of sampling train description components.

Figure 2-3 - Redrawn to show position of thermocouple.

Section 2.2.4 - Clarification of impinger solution description.

Section 3.1 - Changed solvent screening level (acceptable level) from 25 to 5 µg/mL.

Section 4.1.1 - Now includes statement regarding preweighing of filters if particulate is to be measured.

Section 4.1.2 - Now includes statement regarding utilization of retention volumes when selecting the appropriate sample volume.

Section 4.1.3 - Section now discusses use of caustic in the third impinger.

Section 4.1.4.1 - Clarification of leak check procedure.

Section 4.2.3.2 - Clarification of probe rinsing procedure.

Figures 4-2, 4-3, 4-4 - Redrawn with numbering system to indicate the order of sample recovery and to better coordinate the sample description with Table 4-1.

Table 4-1 - Now includes sample numbering system to better coordinate with Figures 4-2, 4-3, and 4-4 and also references to appropriate subsequent sections regarding sample preparations.

Section 4.3.4 - Changed to include weighing of filters prior to extraction.

Section 4.3.5 - Changed to include new preparation procedures for solvent rinses.

Section 4.4.2.2 - Internal (quantitation) standard changed to phenanthrene-d_{10}.

Table 7-1 - Suggested surrogate spiking compounds updated.

Section 7.3.1-2 - Daily calibration changed to a single daily calibration run.

Table 7-2 - Suggested surrogate spiking compounds up-dated.

Table 7-3 - Suggested surrogate spiking compounds up-dated.

Appendix A-2 - Preparation of XAD-2® sorbent resins, last paragraph of Section 2.1 is deleted.

The Semi-VOST sampling and analytical method presented on the following pages incorporates comments and suggestions received from the following companies familiar with the method:

- Entropy Environmentalists, Inc., Raleigh, North Carolina;
- Midwest Research Institute, Kansas City, Missouri;
- PEI Associates, Inc., Cincinnati, Ohio;
- Battelle-Columbus, Columbus, Ohio; and
- GCA, Inc., Boston, Massachusetts.

SAMPLING AND ANALYSIS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. Principal components of the train include a high efficiency glass or quartz fiber filter and a packed bed of porous polymeric adsorbent resin. The filter is used to collect organic ladden particulate materials, and the porous, polymeric resin to adsorb semi-volatile organic species. Semi-volatile species are defined as compounds with boiling points greater than 100°C.

Comprehensive chemical analyses of the collected sample are conducted to determine the concentration and identity of the organic materials.

1.2 Applicability. This method is applicable to the determination of the Destruction and Removal Efficiency (DRE) of semi-volatile Principal Organic Hazardous Compounds (POHC's) from incineration systems.[1] This method also may be used to determine particulate emission rates from stationary sources per U.S. EPA Method 5.[2]

1.3 Method Detection Limit. The overall method detection limits (lower and upper) must be determined on a compound by compound basis as different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrumental minimum detection limit (MDL). Also, the method detection limit must be quoted relative to a given sample volume. The upper limits for the method must be determined relative to compound retention volumes (break-through).

1.4 Method Precision and Bias. The overall method precision and bias must be determined on a compound by compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collect, retention, and extraction efficiency of the train components. From evaluation studies to date using a dynamic spiking system, method biases of -13 and -16 percent have been determined for toluene and 1,1,2,2-tetrachloroethane, respectively. A method precision of 19.9 percent was calculated from a field test data set representing seven degrees of freedom which resulted from a series of paired, unspiked Semi-VOST trains sampling the emissions from a hazardous waste incinerator.

1.5 Interferences. Oxides of nitrogen (NO_x) are possible interferents with the determination of certain water soluble compounds such as dioxane, phenol, and urethane. These compounds may react with NO_x in the presence of moisture and, therefore, reduce their concentration. Other areas of concern which could result in a positive or negative bias are (1) compound stability in methylene chloride, (2) the formation of water soluble organic salts on the resin in the presence of moisture, and (3) the solvent extraction efficiency of water soluble compounds from aqueous media. Use of two or more ions per compound for qualitative and quantitative analysis can overcome interference at one mass. These topics should be addressed on a compound by compound basis before using this method.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 2-1. This sampling train configuration is adapted from EPA Method 5[2] procedures and most of the equipment required is identical to that used in EPA Method 5 determinations. The additional components required are a condenser coil and a sorbent module, which is used to collect semi-volatile organic materials that pass through the glass or quartz fiber filter in the gas phase.

Construction details for the basic train components are given as part of EPA Method 5 in the report by Robert M. Martin;[5] commercial models of this equipment are also available. Specifications for the sorbent module are provided in the following subsections. In addition, the following subsections list changes to the basic system described by Martin, and identify allowable train modifications.

Basic operating and maintenance procedures for the sampling train are described by Jerome J. Rom.[6] As correct usage is important in obtaining valid results, all users should refer to this reference and adopt the operating and maintenance procedures outlined therein, unless otherwise specified. The sampling train consists of the components described in the following paragraphs.

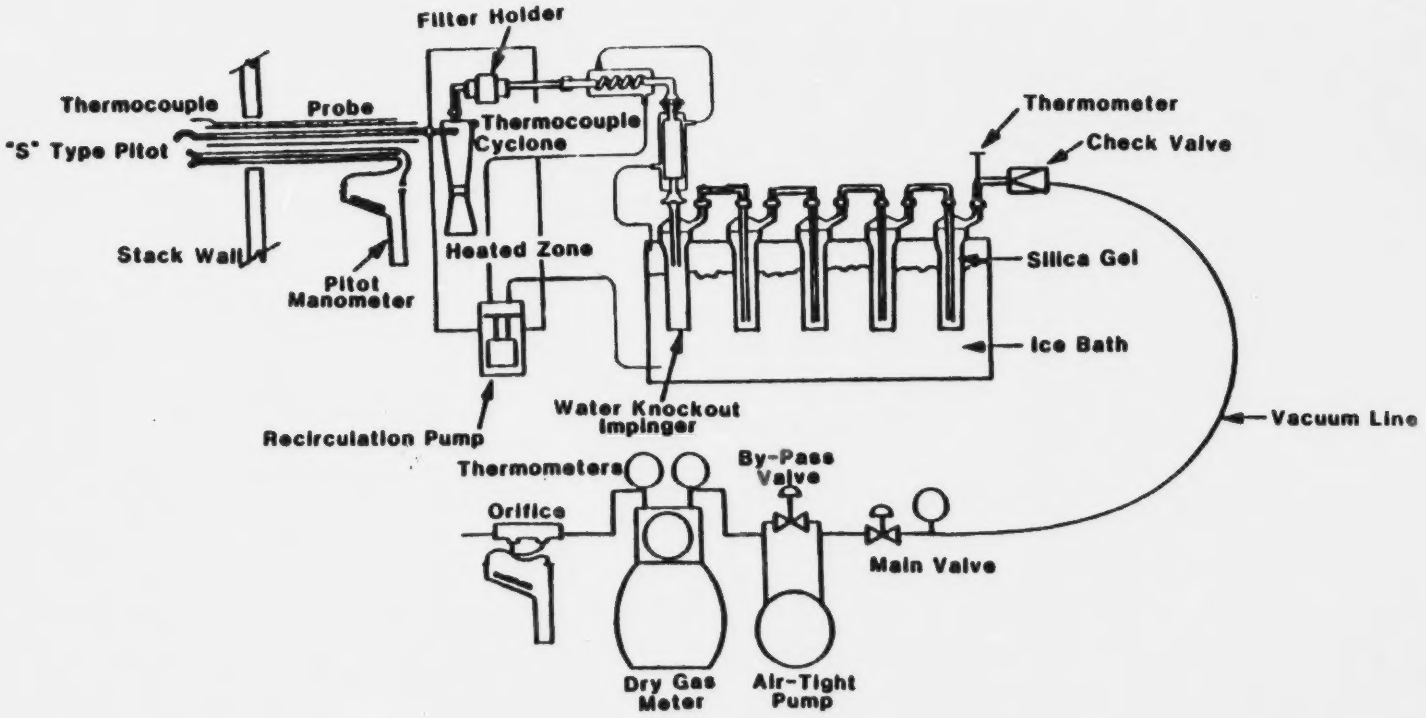
Filter Holder
Thermocouple
Probe
Thermocouple
Cyclone
"S" Type Pitot
Stack Wall
Pitot Manometer
Heated Zone
Thermometer
Check Valve
Silica Gel
Ice Bath
Vacuum Line
Water Knockout Impinger
Recirculation Pump
Thermometers
By-Pass Valve
Orifice
Main Valve
Dry Gas Meter
Air-Tight Pump

Figure 2-1. Semi-VOST train schematic diagram.

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be 30° and the taper shall be on the outside to preserve a constant inside diameter (ID). The probe nozzle shall be the buttonhook or elbow design, unless another configuration is necessary for a special application. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be considered for particular applications.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) inside diameter. If higher volume sampling trains are used, nozzles with ID's increasing in increments of 0.16 cm (1/16 in.) can be procured. Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate glass or quartz tubing with a heating system capable of maintaining a gas temperature of 120 ± 14°C (248 ± 25°F), or such other temperature appropriate for a particular application. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to Martin[5] and utilizing the calibration curves of Rom[6] (or calibrated according to the procedure outlined in Rom) are considered acceptable.

Either borosilicate glass or quartz probe liners may be used for stack temperatures up to about 480°C (900°F). Quartz liners shall be used for temperatures between 480 and 900°C (900 and 1,650°F). Water-cooling of the stainless steel sheath will be necessary, however, at temperatures approaching and exceeding 500°C.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of EPA Method 2[2] or other appropriate[7] devices. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2.

2.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2. One manometer shall be used for velocity head (ΔP) readings, and the other for orifice differential pressure (ΔH) readings.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a sealing gasket. The sealing gasket should be made of material(s) that will not introduce organic material into the gas stream at the temperature at which the filter holder will be maintained. The gasket shall be constructed of Teflon® or materials of equal or better characteristics. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The filter holder shall be attached immediately to the outlet of the cyclone or cyclone bypass.

2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature of 120 ± 14°C (248 ± 25°F) in the vicinity of the filter holder during sampling; other temperatures may be appropriate for particular applications.

2.1.7 Organic Sampling Module. This unit consists of three sections including a gas conditioning section, a sorbent trap and a condensate knockout trap. The gas conditioning system shall be capable of conditioning the gas leaving the back half of the filter holder to a temperature not exceeding 20°C (68°F). The sorbent trap shall be sized to contain approximately 20 grams of porous polymeric resin (Rohm and Haas XAD-2®). The most commonly used coolant is ice water from the impinger ice water bath constantly circulated through the outer jacket using rubber or plastic tubing and a peristaltic pump. The sorbent trap should be outfitted with a glass well or depression, appropriately sized to accommodate a small thermocouple in the trap for monitoring the gas entry temperature. The condensate knockout trap shall be of sufficient size to collect the condensate following gas conditioning. The organic module components shall be oriented to direct the flow of condensate vertically downward from the conditioning section, through the adsorbent medium, and into the condensate knockout trap. The knockout trap is usually similar in appearance to an empty impinger directly underneath the sorbent module; it may be oversized but should have a shortened center stem (at a minimum, one-half the length of the normal impinger stems) to collect a large volume of condensate without bubbling and overflowing into the impinger train. All surfaces of the organic module wetted by the gas sample shall be fabricated of borosilicate glass, Teflon® or other inert materials.

Versions of the complete organic module are not commercially available, but may be assembled from commercially available laboratory glassware and a custom-fabricated sorbent trap. Details of two acceptable designs are shown in Figures 2-2 and 2-3. (The thermocouple well is shown in Figure 2-2).

2.1.8 Impinger Train. The following system shall be used to determine the stack gas moisture content. Following the knockout trap are four 500 mL impingers connected in series with leak-free ground glass joints. The first, third and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to about 1.3 cm. (1/2 in.) from the bottom of the outer cylinder. The second impinger shall be of the Greenburg-Smith design with the standard tip. The first and second impingers shall contain known quantities of water or appropriate trapping solution. The third shall be empty or be charged with a caustic solution should the stack gas contain hydrochloric acid (HCl). The fourth shall contain a known weight of silica gel or equivalent desiccant.

2.1.9 Metering System. The necessary components are a vacuum gauge, a leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), and a dry gas meter capable of measuring volume to within 1 percent, as shown in Figure 2-1. At a minimum, the pump should be capable of 4 cfm free flow and the dry gas meter should have a recording capacity of 0-999.9 cubic feet with a resolution of 0.005 cubic feet. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 1 percent may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

Sampling trains utilizing metering systems designed for higher flow rates than those described by Martin[5] or Rom[6] may be used provided that the specifications of this method are met.

2.1.10 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm. Hg (0.1 in. Hg). The barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric

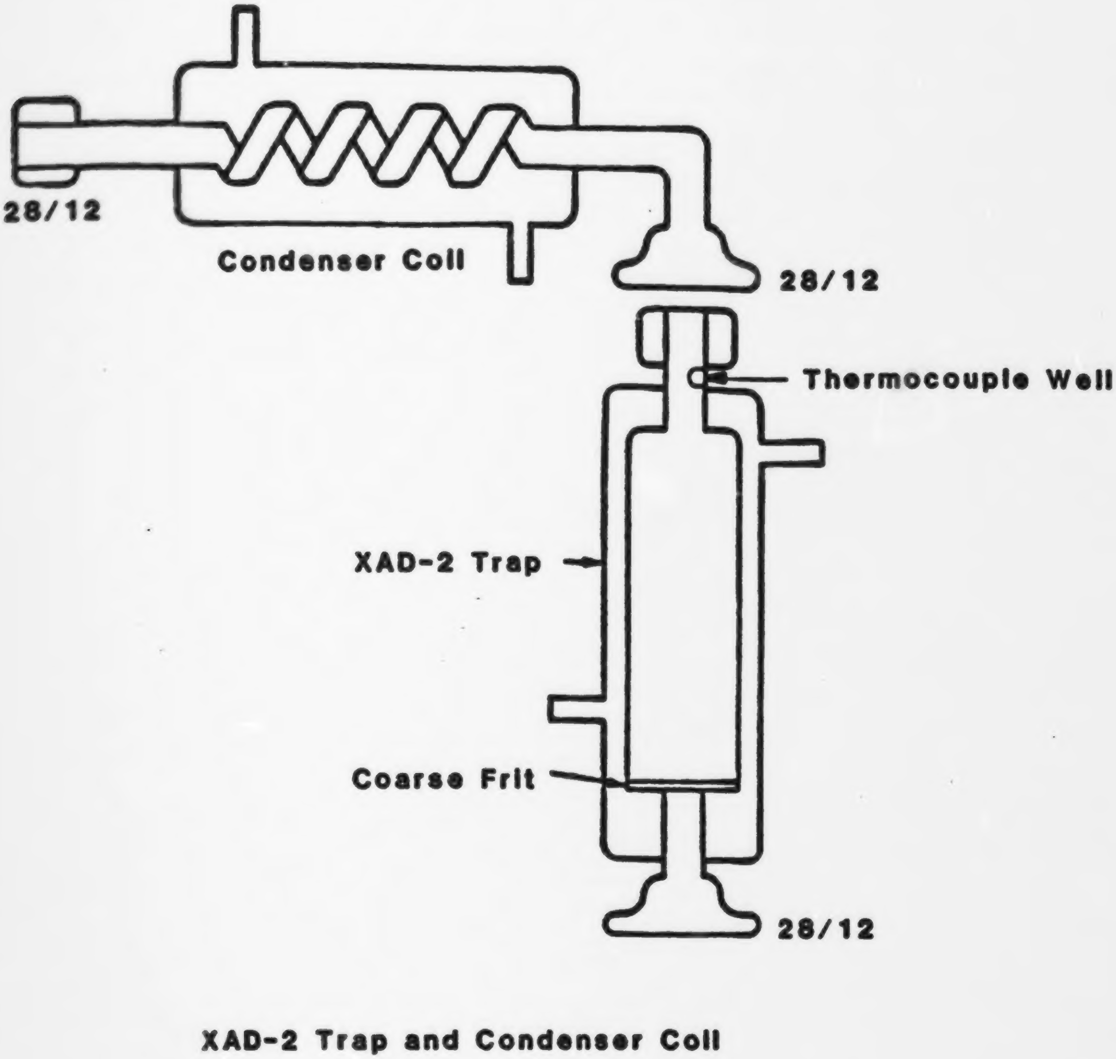
28/12
Condenser Coil
28/12
Thermocouple Well
XAD-2 Trap
Coarse Frit
28/12
XAD-2 Trap and Condenser Coil

Figure 2-2. Acceptable sorbent module design #1.

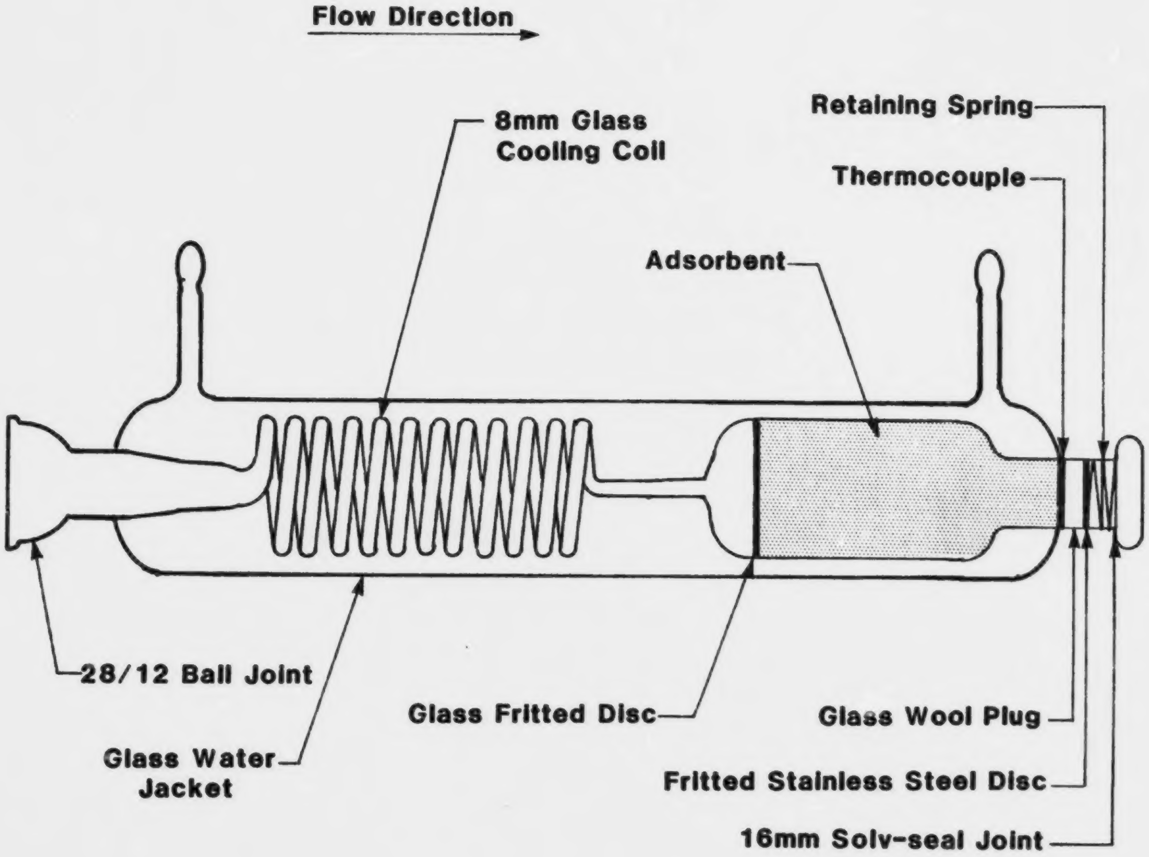
Flow Direction
8mm Glass Cooling Coil
Retaining Spring
Thermocouple
Adsorbent
28/12 Ball Joint
Glass Water Jacket
Glass Fritted Disc
Glass Wool Plug
Fritted Stainless Steel Disc
16mm Solv-seal Joint

Figure 2-3. Acceptable sorbent module design #2.

pressure) shall be requested and an adjustment for elevation difference between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.11 Crushed Ice. Quantities ranging from 10-50 lb may be necessary during a sampling run, depending upon ambient air temperatures.

2.1.12 Glass Wool. Used to plug the unfritted end of the sorbent module. The glass wool fiber should be solvent-extracted with methylene chloride in a Soxhlet extractor for 12 hours and air-dried prior to use.

2.1.13 Gas Density Determination Equipment. The fixed gas samples for determining the stack gas density during the sampling run are taken using an integrated gas sampling train. The gas sample is bled through a nonreactive probe and an air-cooled condenser or equivalent which removes excess moisture from the gas stream and cools the hot gas to ambient temperatures. The sampling flowrate is measured with a flow rate meter and controlled by a needle valve. The sample is collected in a leak-free bag and analyzed with an ORSAT appraratus. Detailed specifications may be found in EPA Method 3.[2]

2.1.14 Calibration/Field Preparation Record. For documenting and recording calibrations and preparation procedures (i.e., filter and silica gel tare weights, clean XAD-2®, quality assurance/quality control check results, dry gas meter and thermocouple calibrations, etc.), a permanently-bound laboratory notebook is required, in which duplicate copies of the data may be made as they are being recorded. The duplicate copies should be detachable and stored separately in the test program archives.

2.2 Sample Collection Media

2.2.1 Filters. Glass or quartz fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) for 0.3 um dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71.[4] Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of type that is unreactive to these acid gases.[3] Reeve Angel® 934 AH or Schleicher and Schwell #3 filters work well under these conditions.

2.2.2 Adsorbent Resin. Porous polymeric resin, XAD-2®, shall be used. The resin must be cleaned prior to use, according to the procedure outlined in Appendix B of this method. Once cleaned, the resin should be stored in an air-tight wide-mouth amber glass container with a Teflon®-lined cap or placed in one of the glass sorbent modules tightly sealed with Teflon® film and elastic bands. The resin should be used within four weeks of the preparation. Additional details are found in Section 3.

2.2.3 Silica Gel. Indicating type, 6 to 16 mesh. Dry at 175°C (350°F) for 2 hours before using.

2.2.4 Impinger Solutions. Distilled organic-free water shall be used to charge the impingers. This water should be prescreened for any compounds of interest. One hundred mL will be added to the specified impinger: the third impinger in the train may be charged with a basic solution (1 N sodium hydroxide or sodium acetate) to protect the sampling pump from acidic gases. Sodium acetate should be used when large sample volumes are anticipated, as sodium hydroxide will react with carbon dioxide in aqueous media to form sodium carbonate and possibly plug the impinger. Additional details are found in Section 3.

2.3 Materials and Supplies Needed for Sample Recovery

2.3.1 Methanol/Methylene Chloride. Methanol and methylene chloride are used for sample recovery and clean-up. Screening details are given in Section 3.

2.3.2 Water. Organic-free water shall be used to aid in quantitatively transferring any impinger solutions that will be analyzed.

2.3.3 Probe Liner, Nozzle and Organic Module Brushes. Nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon®, or inert material equal to the length of the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the nozzle and the organic module conditioning section.

2.3.4 Wash Bottles. Teflon® or glass wash bottles are required; polyethylene wash bottles should not be used as organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

2.3.5 Glass Sample Storage Containers. Chemically resistant, borosilicate amber and clear glass bottles, 500 mL and 1,000 mL. Screw cap liners shall either be Teflon® or otherwise constructed to be leak free and resistant to chemical attack by organic recovery solvents.

2.3.6 Petri Dishes. Glass, sealed around the circumference with wide (1 in) Teflon® tape, for storage and transport of filter samples.

2.3.7 Graduated Cylinder and/or Triple-Beam Balance. To measure condensate water to the nearest 1 mL or 1 gram. Graduated cylinders shall have subdivisions no greater than 2 mL. Laboratory triple-beam balances capable of weighing to ±0.5 gram are required.

2.3.8 Nalgene® Storage Containers. Screw cap polypropylene or polyethylene containers to store silica gel.

2.3.9 Funnels. Glass funnels are required to aid in the recovery of samples for organic analyses.

2.4 Sample Preparation and Analysis

2.4.1 Gas Chromatograph/Mass Spectrometer (GC/MS). A GC/MS coupled to a computer for data acquisition is required for compound identification and quantification. The GC portion of the instrument should be equipped with a fused silica capillary column and be capable of temperature programming. The mode of sample injection should be on-column, but split/splitless injection is acceptable if the split ratio is accurately known giving adequate detectability. Details of the analytical column and analytical parameters are given in Section 4.4.

The MS portion should have at least the following capabilities:

- electron ionization (EI), 70 ev (nominal);
- scanning 35-450 mass units/second;
- single (or selected) ion monitoring; and
- a minimum detectable limit of approximately 25 ng per component on column.

2.4.2 Glassware. All glassware is to be cleaned before use by the procedure given in Appendix A. A "glassware" blank is required for the Soxhlet extractor, empty glass thimble, and concentration apparatus. The blank is prepared by charging the extractor with 300 mL of the sample extraction solvent, cycling the extractor overnight, concentrating the solvent to 1 mL and analyzing by GC/MS as described in Section 4.4. This 1 mL sample should be screened for the compounds of interest. (This assay could also serve as the required screening of the extraction solvent as discussed in Section 3.2.2.) Each Soxhlet set-up should be distinctly marked and should have a corresponding sample concentrator identically marked. These two apparatuses should always be used in pairs to facilitate the identification of any contamination problems. If the glassware blank indicates contamination, a solvent rinse of the entire system should be performed, charged with solvent and again cycled overnight as described above. Continue this process until the blank is free of the components of interest at the minimal detection limit (MDL) of the GC/MS. If contamination persists at the same level, the solvent purity should be investigated.

2.4.2.1 Soxhlet Extractor. Consisting of a 500 mL receiver extractor, condenser, and glass thimble with an extra coarse ground glass-frit.

2.4.2.2 Kuderna-Danish Evaporative Concentrator (K-D). 500 mL size with a 15 mL graduated receiver and a Snyder column. Micro K-D's for reducing sample down to 1 mL.

2.4.2.3 Sample Vials. 2 mL and 10 mL size. Vials should be equipped with Teflon®-lined screw caps.

2.4.2.4 Volumetric Flasks. 10-100 mL size. Used for preparing standards.

2.4.2.5 Funnels. Used for transferring solvent to K-D and containing the desiccant, Na_2SO_4.

2.4.2.6 Glass Wool. Cleaned by Soxhlet extraction for 12 hours with extraction solvent. Used as support for bed of Na_2SO_4 desiccant and to prevent the XAD-2® from floating from the thimble during extraction.

2.4.2.7 Miscellaneous Beakers. 10-400 mL size.

2.4.2.8 Disposable Pipets. For transferring sample to vials.

2.4.2.9 Separatory Funnels. 250 and 500 mL size with Teflon® stopcock.

2.4.2.10 Graduated Cylinders. 100 and 500 mL size.

2.4.3 Syringes. 10 and 100 µL size. Use separate syringes for injecting sample into the GC/MS and spiking surrogate compounds.

2.4.4 Drying Oven. Vacuum or convection type. 0-300°C.

2.4.5 Analytical Balance. Capable of weighing to the nearest 0.1 mg.

2.4.6 Stainless Steel Tongs. For transferring thimble to extractor.

2.4.7 Boiling Chips. Teflon® boiling chips, cleaned in batch quantities by Soxhlet extraction for 12 hours using the sample extraction solvent.

3. Reagents

It is imperative that all reagents be screened for organic pollutants (i.e., compounds of interest or compounds that may interfere with the analysis) by GC/MS before use in either sampling or analytical procedures. Once a particular "lot" has been deemed acceptable by the established criteria, the same lot must be used to complete all analyses.

3.1 Solvents. The solvents used for both the sampling and analysis must be screened prior to use regardless of the indicated purity. Solvents can be purchased and screened by "lot number" thus eliminating the necessity to screen each bottle. Solvents classified as "Distilled in Glass", "Pesticide Grade", "GC/MS Grade", etc. are generally free of most impurities.

Organic solvents are screened by concentrating 500 mL of the solvent to 1 mL and analyzing by GC/MS as described in Section 4.4. The presence of any compound of interest at a level greater than 5 µg/mL (5 ng/µL) in the concentrate will be cause for the rejection of the particular lot number.

Organic-free water is screened by solvent extraction, utilizing a separatory funnel. A 200 mL aliquot is extracted three times with 50 mL portions of pre-screened methylene chloride. The extract is concentrated to 1 mL and analyzed by GC/MS. The presence of any compound of interest at a level greater than 5 µg/mL will be cause for the rejection of the particular lot number.

3.2 Sodium Sulfate (Na_2SO_4). Sodium sulfate is used to remove any traces of water from the solvents before concentration. Reagent grade Na_2SO_4 is cleaned by multiple washings (5-6) with the sample extraction solvent. The cleaned Na_2SO_4 is dried in an oven (vacuum, preferably; convection, alternatively) at 105°C.

3.3 Deionized Organic-Free Water. Water suitable for washing glassware is prepared by first treating with ion-exchange resins followed by charcoal filtration. Water prepared in this manner should exhibit a resistivity in excess of 18 meg-ohms. The organics level is greatly reduced over tap water but the "organic-free" water is generally not free of trace levels of organics. Organic-free water is also commercially available.

3.4 XAD-2® Resin. XAD-2® (20/60 mesh) can be obtained from any of several vendors of chromatography supplies and accessories either precleaned or as supplied by the manufacturer. (Precleaned resin is defined by the procedure given in EPA 600/7-78-201, Appendix B.) Precleaned resin should be screened before use by subjecting a 20 g portion to solvent extraction and analysis procedures. New XAD-2® should be cleaned by the procedure outlined in Appendix B of this method with the final extraction solvent being concentrated and screened for impurities by GC/MS. If the cleanliness criteria are not met, repeat the final extraction step until the criteria are met. If the resin is not deemed "clean" by the third repeat, check for sources of contamination such as glassware and/or solvent. The glassware and solvents can be screened for contaminants by performing an extraction/analysis sequence without the presence of XAD-2®. The final extraction solvent is defined as the solvent to be used to extract the sample components from the XAD-2® after sampling. The resin may be extracted in small batches, individually screened, and then combined (if desired) or extracted in bulk. The cleaned resin can be stored in clean amber jars at room temperature (25°C) or less in an area that has minimal levels of possible contaminants (i.e., do not store in a refrigerated area used to contain samples and/or standards). Alternatively, the resin can be packed in the glass sampling modules and capped. Sampling should be scheduled as soon as possible after resin clean-up has been completed. The shelf life has been determined to be about four weeks. The XAD-2® sampling modules should be shipped to and from the laboratory on ice.

3.5 Standards. Standards, as the neat compound, should be obtained in the purest form available, usually "99+ percent purity." These compounds should also be obtained in the stable isotopic labeled form, if possible, for use as surrogate spikes.

3.6 Nitrogen. High purity nitrogen (see Appendix B) in compressed gas cylinders is required for sample concentration and the removal of solvent from the XAD-2® resin after clean-up.

3.7 Helium. High purity helium (<0.5 ppm total hydrocarbon) in compressed gas cylinders is used as carrier gas for the GC/MS.

4. Procedure

4.1 Sampling.

4.1.1 Pretest Preparation. The complexity of this method is such that, in order to obtain reliable results, field personnel shall be trained in the use of the test procedures. All the components shall be maintained and calibrated according to the procedure described by Rom[6] unless otherwise specified.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in the impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Filters should be preweighed if particulate loading is to be determined. Label the shipping containers (glass petri dishes) and keep the filters in these containers at all times except during sampling.

4.1.2 Preliminary Determination. Select the sampling site and the minimum number of sampling points according to EPA Method 1.[2] Determine the stack pressure, temperature, and the range of velocity heads using EPA Method 2.[2] It is recommended that a leak-check of the pitot lines (EPA Method 2,[2] Section 3.1) be performed. Determine the stack gas moisture content using the EPA Approximation Method 4[2] or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in EPA Method 2,[2] Section 3.6. If the integrated EPA Method 3[2] sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

Select a nozzle size based on the range of preliminary gas stream velocity measurements so that it is not necessary to change the nozzle in order to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocities encountered; see Section 2.2 of EPA Method 2.[2]

Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of the probe.

Typically three (3) dscm (105.9 dscf) of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of POHC's from incineration systems.[10] Additional sample volume shall be collected as necessitated by analytical detection limit constraints. Consideration should also be given to specific retention volume data on a compound by compound basis. If such data are not available, the information must be established for the compound(s) of interest to avoid inaccurate results.

Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate to the volume requirement. Allocate the same time to each traverse point defined by EPA Method 1.[2] The length of time sampled at each traverse point should be an integer or an integer plus one half minute to avoid timekeeping errors.

In some circumstances, (e.g., incinerator waste being fed in batches) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes.

4.1.3 Preparation of the Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon® film or aluminum foil until just prior to assembly or until sampling is initiated.

The XAD-2® sorbent traps are prepared in the laboratory by filling with 20 grams of clean resin. While filling, distribute the resin uniformly to eliminate the possibility of channeling. When freshly cleaned, many adsorbent resins carry a static charge, causing the resin to cling to the trap walls. This may be minimized by filling the trap in the presence of an ionizing source such as Polonium-210 which acts as an antistat to remove the static charge carried by the resin. Commercial antistatic devices are the Model-204®* and Model-210®*, available from the 3-M Company, Inc., St. Paul, MN.

Place 100 mL of distilled-deionized organic-free water in each of the first two impingers following the knockout trap, leave the third impinger empty (or charge with caustic solution as necessary), and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the silica gel plus impinger may be weighed together to the nearest 0.5 g and the weight recorded.

Using tweezers or clean disposable surgical gloves, place a labeled (identified) filter in the filter holder. Be sure that the filter is properly centered and the gasket placed to prevent the sample gas stream from bypassing the filter. Visually check the filter for tears or lifting after assembly is complete.

When glass liners are used, install the selected nozzle using a Viton-A O-ring if stack temperatures are less than 260°C (500°F) and a woven glass fiber gasket when temperatures are higher. See Rom[6] for details. Other connecting systems using either 316 stainless steel or Teflon® ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection.

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*Registered trademarks of the 3-M Company, Inc., St. Paul, MN.

Set up the train as in Figure 2-1. If necessary, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to contain large particles or when water droplets are present in the stack.

Connect all temperature sensors to an appropriate potentiometer/ display unit. Check all temperature sensors at ambient temperature.

Place crushed ice around the impingers and the organic module condensate knockout.

Turn on the sorbent module and condenser coil coolant recirculating pump and begin monitoring the sorbent module gas entry temperature. Insure proper sorbent module gas entry temperature before proceeding and again before any sampling is initiated. It is extremely important that the XAD-2® resin temperature never exceed 50°C (122°F), as thermal decomposition will occur. During testing, the XAD-2® temperature must not exceed 20°C (68°F) for efficient capture of the semivolatile species of interest.

Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. Since the number of additional intercomponent connections in the Semi-VOST train (over the M5 Train) increases the possibility of leakage, a pretest leak-check is required.

A lower vacuum may be used, provided that it is not exceeded during the test. Leak test by first attaching to the inlet of the filter holder (cyclone, if applicable) a carbon-filled leak check impinger shown in Figure 4-1, plugging the inlet and evacuating to 381 mm Hg (15 in Hg). Once the train has passed the leak check criteria, the probe should be connected to the train, the end plugged, and the train leak-checked at 25 mm Hg (1 in Hg). Alternatively, the probe may be leak-checked simultaneously with the rest of the sampling train, in one step, at 381 mm Hg (15 in Hg) vacuum. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, is unacceptable and must be corrected.

CROSS SECTIONAL VIEW

Leak Testing Apparatus

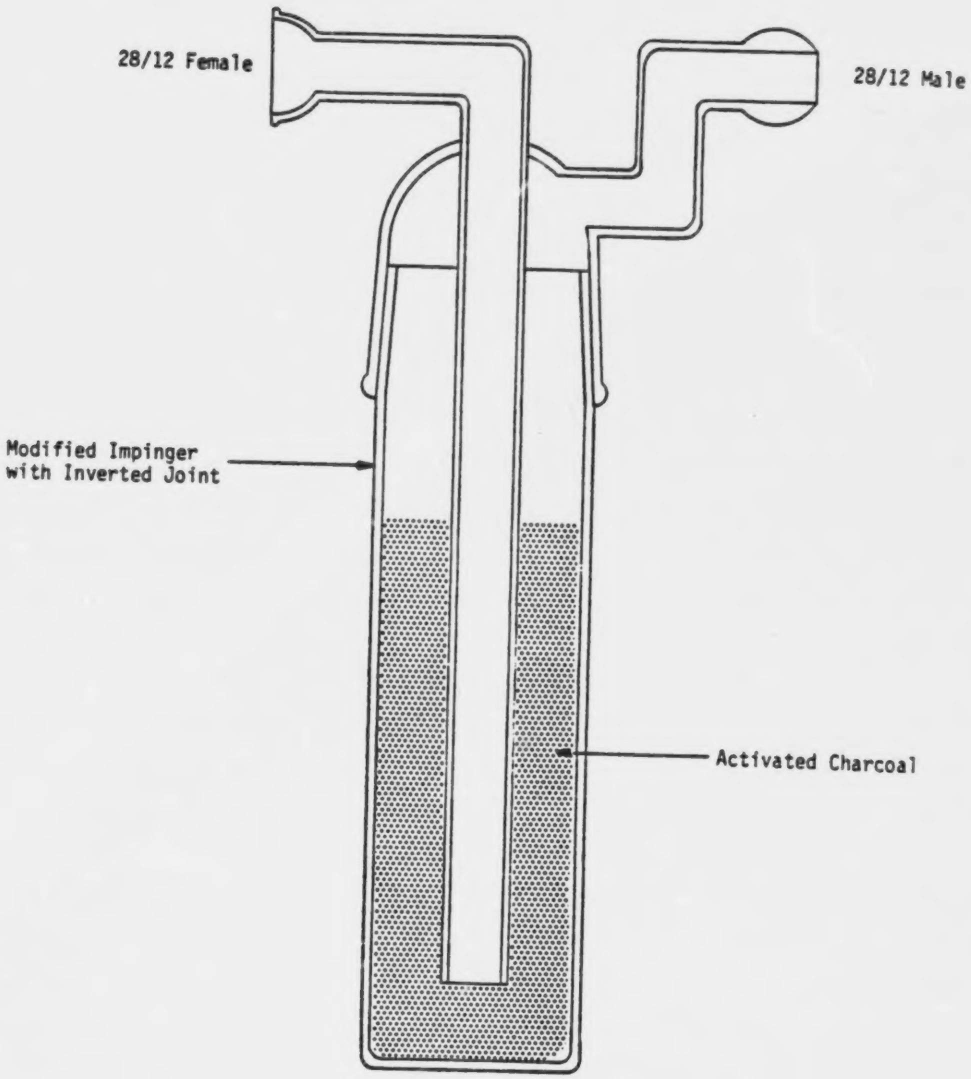

28/12 Female
28/12 Male
Modified Impinger with Inverted Joint
Activated Charcoal

Figure 4-1. Leak check impinger.

These specific leak-testing instructions described in Rom[6] are strongly recommended. Start the pump with fine adjust valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the fine adjust valve until the desired vacuum is reached. Do not reverse direction of the fine adjust valve; this will cause water to back up into the organic module or between the impingers. If the desired vacuum is exceeded, leak-check as instructed below and begin again.

When the leak-check is completed, slowly remove the plug from the inlet to the leak check apparatus. When the vacuum drops to 127 mm (5 in) Hg or less, immediately close the coarse adjust valve. Switch off the pumping system and reopen the fine adjust valve. Do not reopen the fine adjust valve until the coarse adjust valve has been closed to prevent the water in the impingers from being forced backward or the organic module and the silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sampling Run. If during the sampling run, a component (e.g., filter assembly, impinger or sorbent trap) change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 except that it shall be done at a vacuum equal to or greater than the maximum value recorded at that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall void the run unless it is impossible to repeat, in which case he/she shall record the leakage rate and plan to correct the sample volume as shown in Section 6.2 of this method. It should be noted that correction of the sample volume in this manner reduces the integrity of the pollutant concentrations data generated and must be avoided.

Immediately after a component change, and before sampling is re-initiated, a leak-check similar to a pretest leak-check must also be conducted.

4.1.4.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. Use the procedure outlined above insuring that the leak-check is conducted at a vacuum equal to or greater than the maximum value recorded during the sampling run. If the leakage rate is found to be not greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall attempt to repeat the run as previously discussed. If the run cannot be repeated, the tester shall record the leakage rate, correct the volume as shown in Section 6.2 of this method and shall consider the data obtained of questionable reliability.

4.1.5 Sample Collection. During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic. Maintain a temperature around the filter of 120 ± 14°C (248 ± 25°F) and a gas temperature entering the sorbent trap at a maximum of 20°C (68°F).

For each run, record the data required on a data sheet. Take care to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take readings at least once at each sampling point during each time increment. Level and zero the manometer initially and periodically throughout the sampling run.

Clean the stack access ports prior to the test run to eliminate the possibility of sampling deposited material. To begin sampling, remove the nozzle covering, verify that the filter and probe heating systems are at the specified temperature, and that the pitot tube and probe are properly positioned. Place the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.84 ± 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. Rom[6] details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube coefficient are outside the stated ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations.[7]

When the stack is under significant negative pressure (equivalent to the height of impinger stem) take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the organic module. It may be necessary to turn the pump on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and stack accesss port to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by EPA Method 1.[2] Take care not to bump the probe nozzle into the stack walls when sampling near the walls or when removing and inserting the probe through the access port.

During the test run, make periodic adjustments to keep the temperature of the filter holder and the organic module at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20°C (68°F) at the condenser outlet.

If the pressure drop across the filter or sorbent trap becomes too high, making isokinetic sampling rates difficult to maintain, the filter/sorbent trap may be replaced in the midst of a sample run. It is recommended that another complete filter holder/sorbent trap assembly be used rather than attempting to change the filter and resin themselves. After a new filter holder/sorbent trap assembly is installed, conduct a leak-check.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or in cases where equipment failure necessitates a change of trains.

> Note: When two or more trains are used, separate analysis of the front-half (if applicable) organic module and impinger (if applicable) catches from each train may be performed, unless identical nozzle sizes were used on all trains. Then the front-half catches from the individual trains may be combined (as may the impinger

catches) and one analysis of front-half catch and one analysis of impinger catch may be performed.

At the end of the sample run turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check. Leak-check the pitot lines as described in EPA Method 2,[2] Section 3.1. The lines must pass this leak-check in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinecity. Calculate percent isokineticity (see Calculations, Section 6) to determine whether the results are acceptable or whether another test run should be made.

4.2 Sample Recovery.

4.2.1 Disassembly of the Semi-VOST Train. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

4.2.1.1 When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling, as this will create a vacuum in the filter holder drawing water from the impingers back into the sorbent module.

Before moving the sampling train to the cleanup site, remove the probe from the sample train and cap the open outlet, taking care not to lose any condensate that might be present. Cap the filter inlet. Remove the umbilical cord from the last impinger. If a flexible line is used between the organic module and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the organic module.

4.2.1.2 Cap the filter holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas conditioning section. Cap all organic module openings. Disconnect the organic module knockout trap from the impinger train inlet and cap both of these openings. Ground glass stoppers, Teflon® caps or caps of other inert materials may be used to seal all openings.

4.2.1.3 Transfer the probe, the filter, the organic module components and the impinger assembly to the clean-up area. This area should be clean and protected from the elements to minimize sample contamination or loss.

4.2.1.4 Save a portion of all washing solutions (methanol/methylene chloride, distilled-deionized water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle used and place them in separate labeled glass sample containers.

4.2.1.5 Inspect the train prior to and during disassembly and note any abnormal conditions.

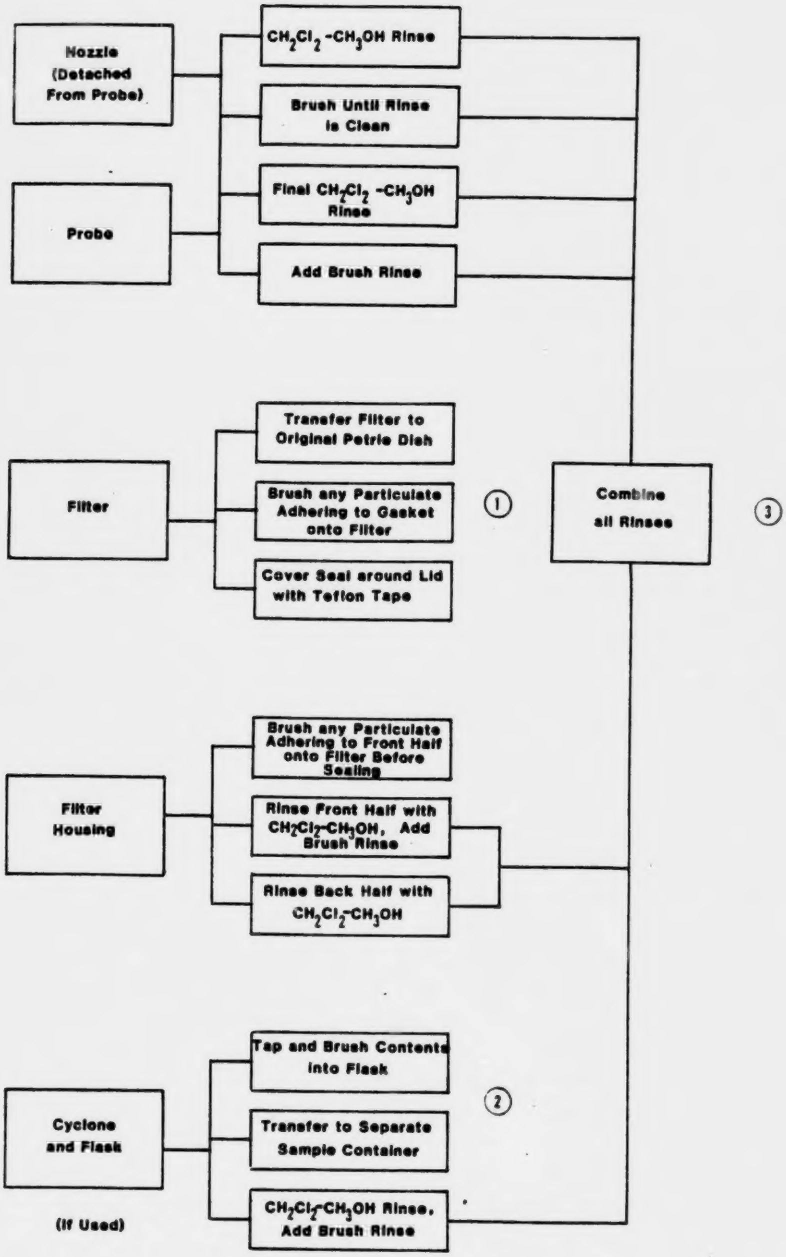
4.2.2 Sample Handling and Transfer. Step-by-step sample handling and transfer procedures are outlined below. Flow diagrams for these recovery procedures are presented in Figures 4-2, 4-3, and 4-4. An example coding format for Semi-VOST samples follows in Table 4-1.

4.2.3 Probe, Nozzle, Cyclone (if used), Filter Recovery.

4.2.3.1 Carefully remove the filter from the filter holder and place it in its identified petri dish. Use two pairs of tweezers to handle the filter. If it is necessary to fold the filter, insure that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, using a dry nylon bristle brush and/or a sharp-edged blade. Label the container and seal with wide (1 in) Teflon® tape around the circumference of the lid.

4.2.3.2 Taking care to see that dust on the outside of the probe or other exterior surfaces does not contaminate the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe liner, and front half of the filter holder by washing these components first with 50 to 75 mL of methanol and then an equal volume of methylene chloride into a glass container. Distilled water may also be used. Retain a water and solvent blank and analyze in the same manner as the samples. Perform rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent mixture (1:1 v/v methanol/methylene chloride) from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particulate material. Then make a final rinse of the inside surface with the solvent mix.


Nozzle (Detached From Probe)
Probe
CH_2Cl_2 -CH_3OH Rinse
Brush Until Rinse is Clean
Final CH_2Cl_2 -CH_3OH Rinse
Add Brush Rinse
Filter
Transfer Filter to Original Petrie Dish
Brush any Particulate Adhering to Gasket onto Filter
Cover Seal around Lid with Teflon Tape
①
Combine all Rinses
③
Filter Housing
Brush any Particulate Adhering to Front Half onto Filter Before Sealing
Rinse Front Half with CH_2Cl_2-CH_3OH, Add Brush Rinse
Rinse Back Half with CH_2Cl_2-CH_3OH
Cyclone and Flask
(If Used)
Tap and Brush Contents into Flask
Transfer to Separate Sample Container
②
CH_2Cl_2-CH_3OH Rinse, Add Brush Rinse

Notes: All Containers for Samples for Organic Analysis must be Glass. Use Teflon or Glass Wash Bottles. Teflon is Preferred.

Figure 4-2. Semi-VOST train sample handling and transfer: nozzle, probe, cyclone (if used) and filter.

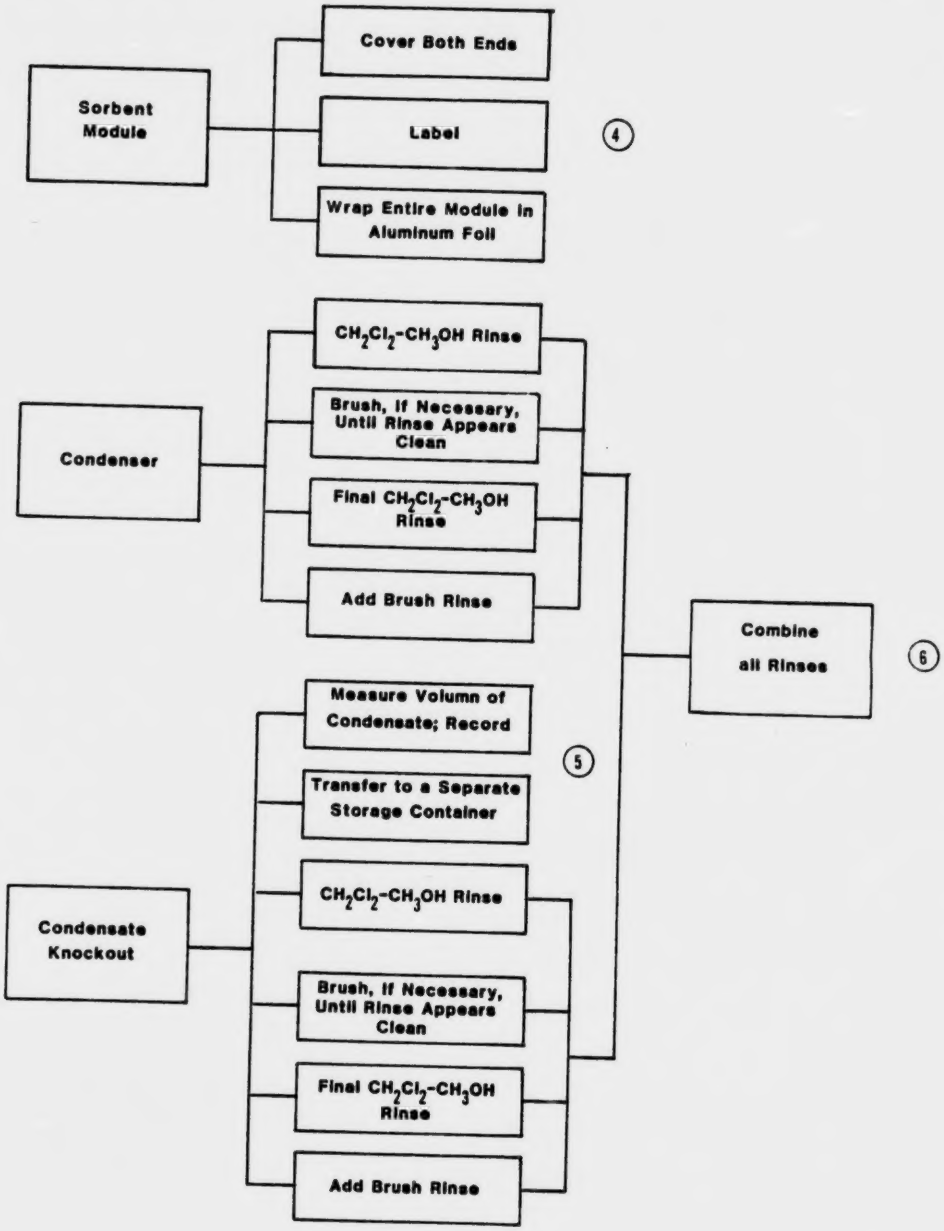

Sorbent Module
Cover Both Ends
Label
Wrap Entire Module in Aluminum Foil
④
Condenser
CH_2Cl_2-CH_3OH Rinse
Brush, If Necessary, Until Rinse Appears Clean
Final CH_2Cl_2-CH_3OH Rinse
Add Brush Rinse
Combine all Rinses
⑥
Condensate Knockout
Measure Volumn of Condensate; Record
Transfer to a Separate Storage Container
⑤
CH_2Cl_2-CH_3OH Rinse
Brush, If Necessary, Until Rinse Appears Clean
Final CH_2Cl_2-CH_3OH Rinse
Add Brush Rinse

Figure 4-3. Semi-VOST train sample handling and transfer: organic module section.

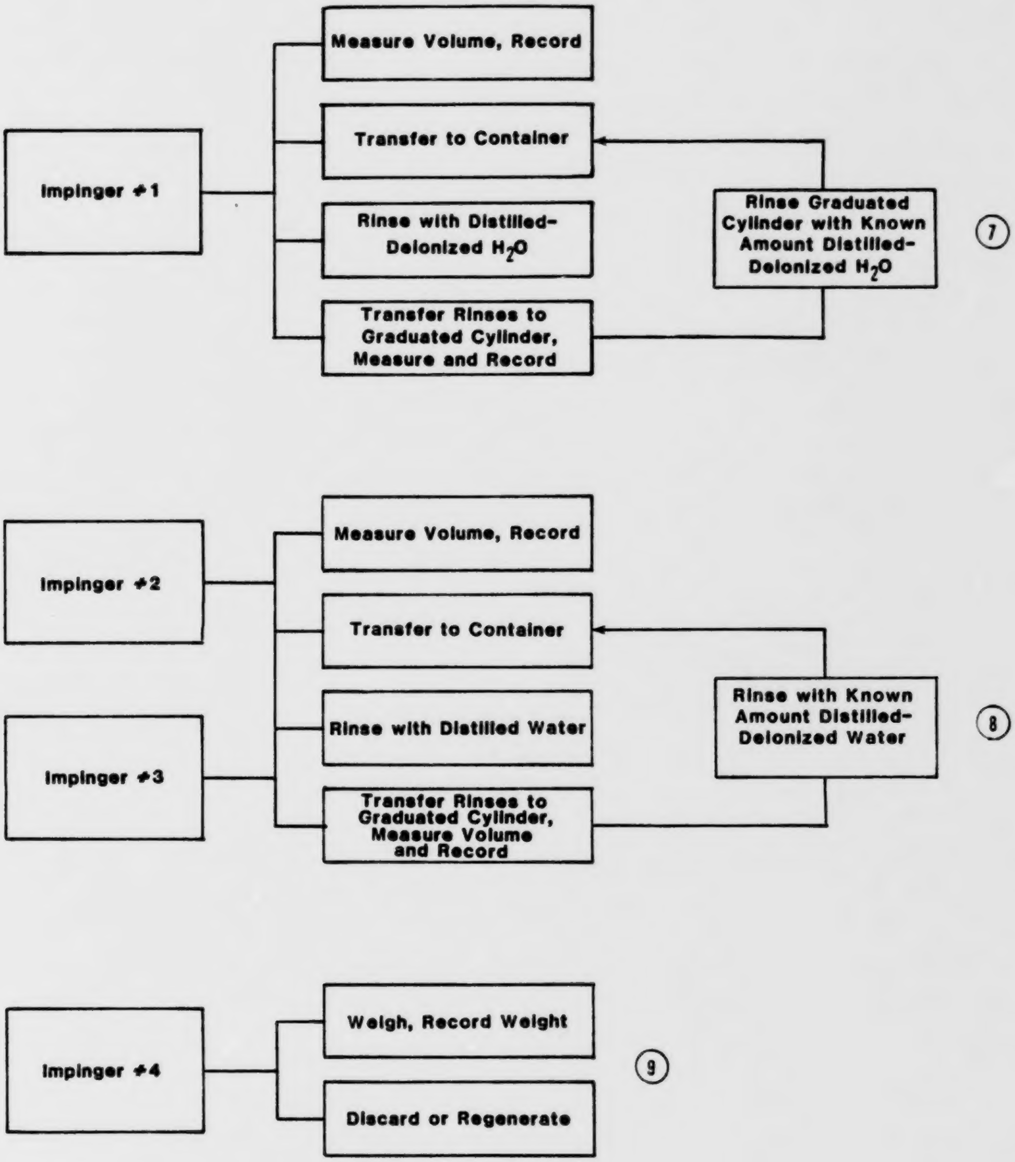

Impinger #1
Measure Volume, Record
Transfer to Container
Rinse with Distilled-Deionized H_2O
Transfer Rinses to Graduated Cylinder, Measure and Record
Rinse Graduated Cylinder with Known Amount Distilled-Deionized H_2O
⑦
Impinger #2
Impinger #3
Measure Volume, Record
Transfer to Container
Rinse with Distilled Water
Transfer Rinses to Graduated Cylinder, Measure Volume and Record
Rinse with Known Amount Distilled-Deionized Water
⑧
Impinger #4
Weigh, Record Weight
Discard or Regenerate
⑨

Figure 4-4. Semi-VOST train sample handling and transfer: impinger train.

Table 4-1. EXAMPLE CODING FORMAT FOR SEMI-VOST TRAIN SAMPLES

Sample code	Order of recovery[a]	Container	Size	Sample preparation[b]	Sample description
PF	1	Glass petri dish(es)	150 mm diameter	4.3.4	Particulate filter(s)
CC	2	Amber glass	100 mL, widemouth	4.3.4	Cyclone catch (if applicable)
FHR	3	Clear glass[c]	1 L	4.3.5	Front-half rinse (50:50 methanol/methylene chloride) i.e., nozzle, probe, filter housing, cyclone
SRB		Clear glass[c]	500 mL	4.3.5	Solvent rinse blank (50:50 methanol/methylene chloride)
XAD	4	Sampling module	100 mL, widemouth or capped sorbent traps	4.3.3	XAD-2® resin sample(s)
CD	5	Amber glass	1 L	4.3.1	Condensate knockout catch
BHR	6	Clear glass[c]	1 L	4.3.5	Back-half rinse (50:50 methanol/methylene chloride) i.e., condenser and knockout traps

(continued)

Table 4-1. Concluded

Sample code	Order of recovery[a]	Container	Size	Sample preparation[b]	Sample description
I-1	7	Amber glass	1 L	4.3.2	First impinger catch and rinse
I-1B		Amber glass	1 L	4.3.2	First impinger blank (appropriate collecting solution)
I-2,3	8	Amber glass	1 L	4.3.2	Second and third impinger catches combined and rinsed
I-2,3B		Amber glass	1 L	4.3.2	Second and third impinger blank (appropriate collecting solution)
I-4	9	Clear glass	1 L	4.2.5	Silica gel

[a] See Figures 4-2, 4-3, and 4-4.

[b] See appropriate sections of the Semi-VOST method.

[c] Must be clear to allow tester to verify when components have been "rinsed clean"; cover with aluminum foil to protect sample from light.

Have two people rinse the probe liner with the solvent mix by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A funnel (glass) may be used to aid in transferring liquid washes to the container. Follow the solvent rinse with a brushing. Both persons should support the probe in an inclined position, while one sprays solvent into the upper end of the liner as the other pushes the probe brush with a twisting action through the probe; the second person must place a sample container underneath the lower end of the probe, and catch any solvent and particulate matter which is brushed from the probe. Run the brush through the probe three or more times until no visible particulate material is carried out with the solvent or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, it is necessary to run the brush through in this manner at least six times since these probes have small crevices in which particulate matter can be entrapped. Rinse the brush with solvent, and quantitatively collect these washings in the sample container. After the brushing, make a final solvent rinse of the probe. Between sampling runs, keep brushes clean and protected from contamination.

4.2.3.3 Clean the inside of the front half of the filter holder and cyclone/cyclone flask, if used, by rubbing the surfaces with a nylon bristle brush and rinsing with methanol/methylene chloride (50:50) mixture. Rinse each surface at least three times to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if used). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all solvent washings and particulate matter have been collected, tighten the sample container lid so that solvent will not leak out upon shipment to the laboratory. Mark the height of the fluid level to allow determination of whether or not leakage occurred during transport. Label the container clearly to identify its contents.

4.2.4 Condenser, Sorbent Module and Condensate Knockout Recovery.

4.2.4.1 The sorbent trap section of the organic module is used as a sample transport container. Ground glass stoppers or Teflon® caps are used to seal the ends. The sorbent trap should then be labeled, covered with aluminum foil and transported to the laboratory on ice.

4.2.4.2 Measure the volume of condensate collected in the condensate knockout section of the organic module to within ±1 mL using a graduated cylinder or by weighing to within ±0.5 g using a triple-beam balance. Record the volume or weight of liquid present, and note any discoloration or film in the liquid catch. Transfer this liquid to a labeled glass container. Inspect the backhalf of the filter housing, and the gas conditioning section of the organic module. If condensate is observed, transfer it to a graduated or weighing bottle and measure the volume as described above. Add this material to the condensate knockout trap catch.

4.2.4.3 All sampling train components located between the high efficiency glass or quartz fiber filter and the first wet impinger (including the heated Teflon® line connecting the filter outlet to the condenser) should be thoroughly rinsed with methanol/methylene chloride (50:50) mixture, and the rinsings combined. The rinsings shall be separated from the condensate. Whenever train components are brushed, the brush should be subsequently rinsed with solvent mixture and the rinsings added to the appropriate sample.

4.2.5 Silica Gel and Impingers Recovery.

4.2.5.1 Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may facilitate pouring the silica gel without losses. A rubber policeman may be used to aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids in the transfer. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

4.2.5.2 Recover the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ±0.5 g by using a triple-beam balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Amber glass containers are used for storage of the impinger catches.

4.2.6 Sample Preparation for Shipment. Prior to shipment recheck all sample containers to insure that the caps are well-secured. Seal the lids of all containers around the circumference with Teflon® tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward. The particulate filters should be shipped unrefrigerated.

4.3 Sample Preparation for Analysis. The preparation steps for all samples will result in a finite volume of concentrated solvent. The final sample volume (usually in the 1-10 mL range) is then subjected to analysis by GC/MS. All samples should be inspected and the appearance documented. All samples are to be spiked with surrogate standards as received from the field prior to any sample manipulations. The spike should be at a level equivalent to 10 times the MDL when the solvent is reduced in volume to the desired level (i.e., 10 mL). The spiking compounds should be the stable isotopically labeled analog of the compounds of interest or a compound that would exhibit properties similar to the compounds of interest, be easily chromatographed, and not interfere with the analysis of the compounds of interest. Suggested surrogate spiking compounds are: deuterated napthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and carbon-13-labeled pentachlorophenol.

4.3.1 Condensate. The "condensate" is the moisture collected in the first impinger following the XAD-2® module. Spike the condensate with the surrogate standards. The volume is measured and recorded and then transferred to a separatory funnel. The pH is to be adjusted to pH 2 with 6 N sulfuric acid if necessary. The sample container and graduated cylinder are sequentially rinsed with three successive 10 mL aliquots of the extraction solvent and added to the separatory funnel.

The ratio of solvent to aqueous sample should be maintained at 1:3. Extract the sample by vigorously shaking the separatory funnel for five minutes. After complete separation of the phases, remove the solvent and transfer to a K-D, filtering through a bed of precleaned, dry sodium sulfate. Repeat the extraction step two additional times. Adjust the pH to 11 with 6 Nsodium hydroxide and re-extract combining the acid and base extracts. Rinse the sodium sulfate into the K-D with fresh solvent and discard the desiccant. Add Teflon® boiling chips and concentrate to 10 mL by reducing the volume to slightly less than 10 mL and then bringing to volume with fresh solvent. In order to achieve the necessary detection limit, the sample volume can be further reduced to 1 mL by using a micro column K-D or nitrogen blow-down. Should the sample start to exhibit precipitation, the concentration step should be stopped and the sample redissolved with fresh solvent taking the volume to some finite amount. After adding a standard (for the purpose of quantitation by GC/MS) the sample is ready for analysis as discussed in Section 4.4.

4.3.2 Impinger Contents. Spike the sample with the surrogate standards, measure and record the volume and transfer to a separatory funnel. Proceed as described in Section 4.3.1.

4.3.3 XAD-2®. Spike the resin directly with the surrogate standards. Transfer the resin to the all glass thimbles by the following procedure. (Care should be taken so as not to contaminate the thimble by touching it with anything other than tweezers or other solvent-rinsed mechanical holding devices.) Suspend the XAD-2® module directly over the thimble. The glass frit of the module (see Figure 2-2) should be in the up position. The thimble is contained in a clean beaker which will serve to catch the solvent rinses. Using a Teflon® squeeze bottle, flush the XAD-2® into the thimble. Thoroughly rinse the glass module with solvent into the beaker containing the thimble. Add the XAD-2® glass wool plug to the thimble. Cover the XAD-2® in the thimble with a precleaned glass wool plug sufficient to prevent the resin from floating into the solvent reservoir of the extractor. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. If a question arises concerning the completeness of the extraction, a second extraction without a spike is advised. The thimble is placed in the extractor and the rinse solvent contained in the beaker is added to the solvent reservoir. Additional solvent is added to make the reservoir approximately two-thirds full. Add Teflon® boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle 5-6 times per hour. Extract the resin for 16 hours. Transfer the solvent and three 10-mL rinses of the reservoir to a K-D and concentrate as described in Section 4.3.1.

4.3.4 Particulate Filter (and cyclone catch). If particulate loading is to be determined, weigh the filter (and cyclone catch, if applicable). The particulate filter (and cyclone catch, if applicable) is transferred to the glass thimble and extracted simultaneously with the XAD-2® resin.

4.3.5 Train Solvent Rinses. All train rinses, (i.e., probe, impinger, filter housing) using the extraction solvent and methanol are returned to the laboratory as a single sample. If the rinses are contained in more than one container the intended spike is divided equally among the containers proportioned from a single syringe volume.

Transfer the rinse to a separatory funnel and add a sufficient amount of organic-free water so that the methylene chloride becomes immiscible and its volume no longer increases with the addition of more water. The extraction and concentration steps are then performed as described in Section 4.3.1.

4.4 Sample Analysis. The primary analytical tool for the measurement of emissions from hazardous waste incinerators is GC/MS using fused silica capillary GC columns. Because of the nature of GC/MS instrumentation and the cost associated with sample analysis pre-screening of the sample extracts by gas chromatography/flame ionization detection (GC/FID) or with electron capture GC/ECD is encouraged. Information regarding the complexity and concentration level of a sample prior to GC/MS analysis can be of enormous help. This information can be obtained by using either capillary columns or less expensive packed columns. However, the FID screen should be performed with a column similar to that used with the GC/MS. Keeping in mind that GC/FID has a slightly lower detection limit than GC/MS, the concentration of the sample can be adjusted either up or down prior to analysis by GC/MS.

The mass spectrometer will be operated in a full scan (40 to 450) mode for most of the analyses. The range for which data are acquired in a GC/MS run will be sufficiently broad to encompass the major ions, as listed in Appendix C of this document, for each of the designated POHCs in an incinerator effluent analysis.

For most purposes, electron ionization (EI) spectra will be collected since a majority of the POHCs give reasonable EI spectra. Also, EI spectra are compatible with the NBS Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions will be used to elucidate molecular weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification.

4.4.1 GC Conditions. The GC should be equipped with fused silica capillary columns for compound separation. Fused silica columns provide the compound separation often necessary for accurate quantitation of a complex sample. Additionally, the inertness of the column itself greatly improves the versatility for samples that contain both polar and non-polar compounds. The conditions for the GC are given below.

- Column: 30 m x 0.32 mm ID fused silica capillary (1 μ film thickness), coated with SE-54 or equivalent.
- Injector Temperature: 280°C.
- Column Temperature: 40°C for 4 minutes then 40-270°C @ 10°/minute. Hold at 270°C until no evidence of eluting peaks.
- Carrier Gas: High purity He flowing @ 1 mL/minute.
- Injection Volume: 1 μL.
- Electron Energy: 70 eV (nominal).

The injection system can be either on-column or split/splitless. The column performance should be checked at least weekly by injecting a test mixture (such as a Grob mix) commercially available from suppliers of chromatography accessories.

The temperature program may be changed if required to accomplish a difficult separation.

4.4.2 MS Conditions. In general, the cycle time between collections of complete mass spectra needs to be selected to be compatible with elution of the components in the sample. For capillary column GC separations, the cycle time will be on the order of one second. Longer cycle times may lead to distortion of the spectra. To adequately characterize a GC peak, at least five spectra will be collected across the peak. For low level components in the extract, the elution peak may be less than 3 seconds wide and it might not be possible to collect enough scans to characterize the GC peak, if the scan repetition rate were greater than 1 second.

To insure consistency with sources of mass spectra, the GC instrumentation will be tuned to meet the spectral criteria for decafluorotriphenylphosphine. The criteria for meeting the tuning requirements are found in EPA Federal Register Method 625 and summarized in Table 4-2.

Typical MS conditions are given as follows.

- Scan Range: 40 to 450 amu.
- Scan Rate: 1 scan/second.

4.4.2.1 Qualitative Identification. The identification of organic POHCs is based both on the chromatographic elution of those compounds and on the specificity of the detection system. The relative retention time of a POHC compared to an appropriate internal standard is generally constant to within about ±0.2 percent, depending upon the compound. For GC/MS, a match in both the relative retention time for the POHCs and the simultaneous elution of multiple analytical ions specific to that POHC will serve to establish the qualitative identification of the components of the sample.

For directed analyses, where specific POHCs are to be measured in the sample, the identification criteria to confirm the presence of a POHC by MS are that the GC retention time for the suspect peak relative to some standard match that for the corresponding POHC and that the characteristic ions of the suspected POHC are present in the unknown

Table 4-2. TUNE CRITERIA FOR DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

Mass	Ion abundance criteria[a]
51	30 to 60
68	<2% of mass 69
70	<2% of mass 69
127	40 to 60
197	<1
198	100 (base peak)
199	5 to 9
275	10 to 30
365	>1
441	Present, but less than mass 443
442	>40
443	17% to 23% of mass 442

[a] All values in percent abundance relative to mass 198, unless otherwise stated.

sample at approximately the same ratio as is present in the standard and that those ions coelute. For those POHCs which may be analyzed with MS detection, Appendix C lists the characteristic ions for use with either electron or chemical ionization.

A key factor in the use of computerized mass spectral search systems is the data base. Ideally, the data base would include spectra of all of the potential compounds of interest and would have been obtained under the same conditions for the GC and the MS as for the incinerator process samples. As a practical alternative, the NBS data base will be used and supplemented with spectra for those POHC compounds which are not in the library, preferably obtained on the instrument to be used for the sample analysis.

A second key factor in the use of computerized mass spectral search systems is the assessment of the confidence to be placed in a qualitative compound identification or "match" with the reference spectrum in the library. The computerized search system typically generates one or more numerical indicators of the "goodness of fit." In the Finnigan INCOS data system, for example, goodness of fit is indicated by three values:

- the fit - how well each library entry is represented in the sample spectrum;
- the reverse fit - how well the sample spectrum is represented in each library entry; and
- the purity - how well both the fit and the reverse fit match the sample spectrum and the library entry.

Of these terms, the purity is the most powerful since a high purity value indicates that both the library entry and the sample spectrum match each other closely and either spectrum accounts for virtually all of the other spectrum. When using a Finnigan INCOS GC/MS/DS, it would be appropriate to base qualitative compound identifications of POHCs on the purity value. For purity values in excess of 900 on the 0 to 1,000 scale, the computer search could be regarded as having identified a single component in the GC peak. A list of the top 5 to 9 choices can also be retrieved as output from the search system. If several compounds are identified with purity values that are close to one another, the analyst should retrieve and examine the library spectra and use the elution order data to ascertain the best candidate for the identity of the GC peak of interest. Similarly, if the purity value has decreased below the 900 value threshold, the analyst should retrieve and examine the library spectra, the sample spectrum, and any retention time data to identify the sampling compound.

The algorithms for calculating "goodness of fit" parameters and the numerical values that are associated with specific levels of confidence in the identification will vary depending on the particular software in the GC/MS system employed for analysis. For this reason, and also because the professional judgment of the mass spectrometrist is an essential element in the qualitative compound identification process, it is not appropriate to specify in this document numerical goodness of fit criteria to be applied to all POHC analyses.

It is essential, however, that all compound identifications be reported with an indication of the goodness of fit criteria that were used in making the assignment. These may include numerical values of parameters from the computerized search system and/or the analyst's professional judgment (e.g., "strong", "probable", "tentative"). Of course, elution order retention time and accordance with the reference spectrum must be utilized to assure correct identification of any and all POHCs in samples from the emissions of hazardous waste incinerators.

4.4.2.2 Quantitation. Prior to analysis, each sample is spiked with a known amount of the internal standard. The response ratio (or factor) of the internal standard (phenanthrene-d_{10}) to the compounds of interest in the sample is then compared to a similar ratio established utilizing an instrument calibration.

The response factor calibration for the individual compounds is established by using a five-point calibration curve with nominal compound levels of 10, 25, 100, 250, and 500 µg/mL. This calibration is established using the compounds of interest at concentrations that will bracket the working range of the anticipated sample concentrations. Sample concentrations can be modified either up or down to fit this range. The quantitation standard will be spiked into the samples so the concentration will fall within the calibration curve.

Calibration methods, using either the raw response of a standard or the relative response of the analyte versus an internal standard as a function of the amount of analyte, are widely used in analytical chemistry for quantification. For these methods, a series of calibration standards is prepared from reagent material of the compound(s) of interest which span the linear working range. Each of these standards is analyzed using the same conditions as would be used for the actual samples. The response-concentration data pairs are combined into a calibration curve by regression or other methods. The level of the compound in the sample is determined by interpolation within the calibration curve. This method is routinely used for GC/MS.

Direct quantification procedures are recommended for any species which are identified in the hazardous waste incinerator samples. However, direct quantification may not be possible due to a shortage of reference standards, etc., and indirect methods may be necessary in some cases. The most common of the indirect methods is to use the response characteristics of a chemically similar compound to estimate the level of the target constituent of interest. Thus, if for example, benzofluoranthenes were unexpectedly found in a sample but no standard were available, then the level of benzofluoranthenes present in the sample might be estimated from the response curve of benzo(a)pyrene, benzo(e)pyrene, or perylene. Chemical similarity includes similar functionalities, isomeric structures, and homologous series of compounds. The quantitative estimates by this method will be of increasing accuracy as the chemical structure of the reference compound approaches that of the compound of interest. Details of the calibration procedure and calculations are given in Section 5.4 and 6, respectively.

5. Calibration

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm. (0.001 in.). Measure the diameter of the nozzle face opening in 3 separate places (i.e. across 3 different diameters) and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm. (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube/Probe Assembly. The Type S pitot tube probe assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2,[2] or assigned a nominal coefficient of 0.84 if it is not visibly nicked, dented or corroded, and meets design and intercomponent spacing specifications.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in Rom.[6] It is recommended that a leak-check be conducted before calibrating the metering system. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. In these cases the following leak-check procedure is suggested: Make a 10-minute calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm). Alternatively, the following procedure is suggested (see Figure 5-1): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in) of water by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in Rom.[6]

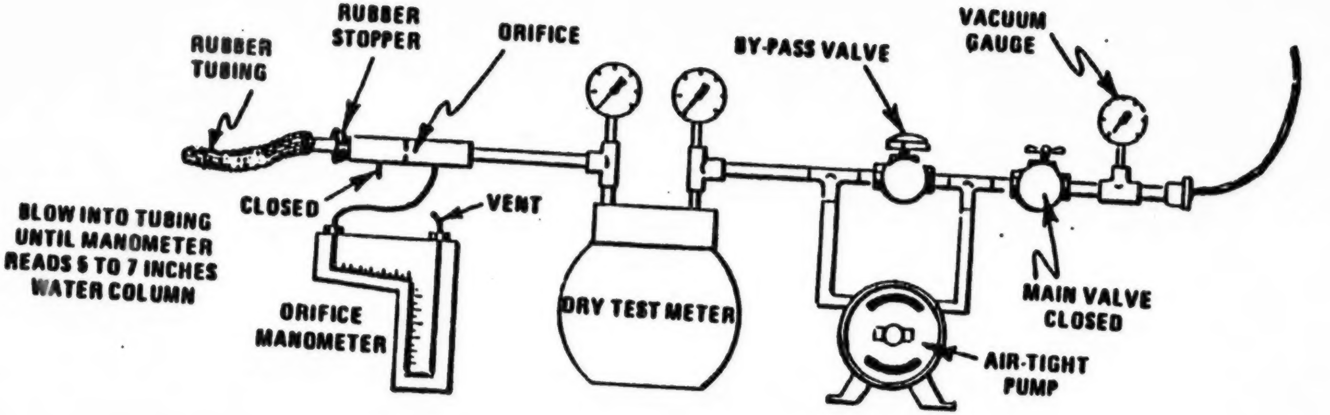

RUBBER TUBING
RUBBER STOPPER
ORIFICE
BY-PASS VALVE
VACUUM GAUGE
CLOSED
VENT
BLOW INTO TUBING UNTIL MANOMETER READS 5 TO 7 INCHES WATER COLUMN
ORIFICE MANOMETER
DRY TEST METER
MAIN VALVE CLOSED
AIR-TIGHT PUMP

Figure 5-1. Meter box leak-check apparatus.

Note: If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Heater. The probe heating system shall be calibrated before its initial use in the field according to the procedure outlined in Rom.[6] Probes constructed according to Martin[5] need not be calibrated if the calibration curves in Rom[6] are used.

5.5 Temperature Gauges. Each thermocouple must be permanently and uniquely marked on the casing; all mercury-in-glass reference thermometers must conform to ASTM E-1 #63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple reading at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change greater than 1.5 percent.

5.5.1 Impinger, Organic Module and Dry Gas Meter Thermocouples. For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2® resin bed, a three-point calibration at ice water, room air and boiling water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ±2°C (3.6°F) with those of the absolute value of the reference thermometer.

5.5.2 Probe and Stack Thermocouple. For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice water, boiling water and hot oil bath temperatures must be performed; it is recommended that room air temperature be added as a thermometer and the thermocouple agree to within 1.5 percent at each of the calibration points. A calibration curve (equation) may be constructed (calculated), and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

5.6 Aneroid Barometer. Adjust the barometer initially and before each test series to agree to within ±2.5 mm Hg (0.1 in Hg) of the mercury barometer, or the corrected barometric pressure value reported by a nearby National Weather Service station. (Same altitude above sea level.)

5.7 Triple-Beam Balance. Calibrate the triple beam balance before each test series using Class-S standard weights; the weights must be within ±0.5 percent of the standards, or the balance adjusted to meet these limits.

5.8 GC/MS. Calibration standards are prepared fresh weekly and run daily. The results are compared to previous runs of the standard (see Section 7, Quality Control for details).

A stock standard is prepared by accurately transferring a known amount of pure compound(s) to a volumetric flask and diluting with methanol. Liquid standards are measured using microliter syringes while solids are conveniently weighed on an analytical balance. The amount (mass) contained in the syringe can be determined by either 1) weighing or 2) utilizing compound density data and the volume. Utilizing the syringe volume method is the most convenient, but care should be excercised to ensure that the most accurate sample is measured. The pure liquid standards should be at room temperature (because most density measurements are made at 20-25°C) and the total syringe volume used should be no less than 10 µL. Care should also be taken not to allow the syringe to warm up (due to body heat) as this will effect the visible measurement of syringe volume. The stock standards should contain all components of interest as well as the compound to be used as the internal standard (see Section 4.4).

Working standards are prepared by diluting aliquots of the stock standard with methanol or other suitable solvent. Again, small volumes are to be avoided, thereby enhancing the accuracy. A calibration curve is developed using a minimum of five standards plus a blank solvent covering a 10-fold range in concentration. This range will be 0 (blank) 0.5X, X, 2X, 5X, and 10X, where X is the minimal detectable amount.

All standards will be stored at sub-ambient temperature and allowed to warm to room temperature before use. Example calculations are given in Section 6.

6. Calculations

6.1 Nomenclature.

A_n = Cross sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak check conducted prior to the i^{th} component change (i=1, 2, 3.....n) m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m^3/min (cfm).

M_d = Stack gas dry molecular weight, g/g-mole (lb/lb-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lbs/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in Hg).

P_s = Absolute stack gas pressure, mm Hg (in Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (21.85 in Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole, (21.85 in Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature, °K (°R).

T_s = Absolute average stack gas temperature, °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{lc} = Total volume of liquid collected in the organic module condensate knockout trap, the impingers and silica gel, mL.

V_m = Volume of gas sample as measured by dry gas meter, m^3 (ft^3).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by EPA Method 2,[2] Equation 2-9, using particulate field data, m/sec (ft/sec).

Y = Dry gas meter calibration factor, dimensionless.

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

Θ = Total sampling time, min.

Θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

Θ_i = Sampling time interval between two successive component changes beginning with the interval between the first and second changes, min.

Θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Conversion to mm Hg (in Hg) from mm H_2O (in H_2O).

60 = Sec/min.

6.2 Dry Gas Volume at Standard Conditions. Correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in Hg) by using the equation:

$$V_{m(std)} = V_m Y \quad \frac{T_{std}}{T_m} \times \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}$$

$$= K_1 V_m Y \quad \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

where:

K_1 = 0.3858 °K/mm Hg for metric units.
= 17.64 °R/in Hg for English units.

Note: This equation can be used as written unless the leakage rate observed during any of the leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, the above equation must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m with the expression:

$$[V_m - \Theta\ (L_p - L_a)]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m by the expression:

$$[V_m - \Theta_1\ (L_1 - L_a)] - \sum_{i=2}^{n} [\Theta_i\ (L_i - L_a) - \Theta_p\ (L_p - L_a)]$$

and substitute only those leakage rates (L_i or L_p) which exceed L_a.

6.3 Moisture Content.

6.3.1 Volume of Water Vapor.

$$V_{w(std)} = V_{1c} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2\ V_{1c}$$

where:

K_2 = 0.001333 m^3/mL for metric units.
= 0.04707 ft^3/mL for English units.

6.4 Isokinetic Variation.

6.4.1 Calculation from Unreduced Data.

$$I = \frac{100\ T_s\ [K_3 F_{1c} + (V_m/T_m)\ (P_{bar} + \Delta H/13.6)]}{60\Theta V_s P_s A_n}$$

where:

K_3 = 0.003454 mm Hg-m^3/mL-°K for metric units.
= 0.002669 in Hg-ft^3/mL-°R for English units.

6.4.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \Theta A_n P_s 60 (1-B_{ws})}$$

$$= \frac{T_s V_{m(std)}}{P_s v_s A_n \Theta (1-B_{ws})}$$

where:

K_4 = 4.320 for metric units.
= 0.09450 for English units.

6.4.3 Acceptable Results. If 90 percent $\leq I \leq 110$ percent, the results are acceptable.

6.5 Concentration of Any Given POHC Per Sample. An average relative response factor (RRF) for a given internal standard is calculated in the following way.

1) Obtain an area count for each compound from injections of each of the five levels of calibration standards. Each standard contains a known amount of the POHC's of interest plus a known amount of the quantitation standard. The area for each compound is based on a preselected ion (usually the major ion). For the quantitation standard, d_{10}-phenanthrene, the major ion is 188.

2) Calculate a relative response factor in triplicate for each compound at each concentration level using the equation below.

$$\mathrm{RRF} = \frac{A_s C_{is}}{A_{is} C_s}$$

where:

A_s = Area of the characteristic ion for the POHC to be measured.
A_{is} = Area of the characteristic ion for the internal standard.
C_{is} = Concentration of the internal standard (μg/mL).
C_s = Concentration of the POHC (μg/mL) to be measured.

3) Average the average RRF's for each compound from each level calculating a grand average RRF for each compound. If RRF mean exhibits a % CV >0, a linear regression may be used.

The concentration of any give POHC is calculated using the equation given below:

$$\frac{C_{is}}{A_{is}\ \text{(major ion)}} \times \frac{A_{unk\ \text{(major ion)}}}{\mathrm{RRF}} = C_{unk}(\mu g/mL)$$

where:

A_{unk} = Area of the major ion for the POHC of interest.
A_{is} = Area of the major ion for the internal standard.
C_{is} = Concentration of the internal standard spiked into the sample (µg/mL).
C_{unk} = Concentration of the unknown (µg/mL).
RRF = Average relative response factor of the POHC of interest.

6.6 Concentration of any Given POHC in the Gaseous Emissions of a Combustion Process.

1) Multiply the concentration of the POHC as determined in Section 6.5 by the final concentration volume, typically 10 mL.

$$C_{unk}\ (\mu g/mL) \times \text{sample volume (mL)} = \text{amount } (\mu g) \text{ of POHC in sample}$$

2) Sum the amount of POHC found in all samples associated with a single train.

$$\text{Total } (\mu g) = \text{XAD-2}^{\circledR}\ (\mu g) + \text{condensate } (\mu g) + \text{rinses } (\mu g) + \text{impinger } (\mu g)$$

3) Divide the total µg found by the volume of stack gas sampled (m^3).

$$\text{Total } \mu g/\text{train sample volume} = \text{concentration of POHC } (\mu g/m^3)$$

6.7 Percent Recovery. Divide the amount of any single surrogate spiked into a sample before sample work-up into the amount of that surrogate found to be in sample after analysis. Then convert to a percent.

$$\frac{\text{Amount of spike found after analysis}}{\text{Amount of spike into a sample}} \times 100 = \%\ \text{recovery.}$$

7. Quality Control.

Table 7-1 presents the major components of the quality control for this method.

7.1 Sampling. See EPA Manual 600/4-77-027b for Method 5 quality control.

7.2 Analysis. The quality assurance program required for this study includes the analysis of field and method blanks, procedure validations, incorporation of stable labeled surrogate compounds, quantitation versus stable labeled internal standards, capillary column performance checks and external performance tests. The surrogate spiking compounds selected for a particular analysis are used as primary indicators of the quality of the analytical data for a wide range of compounds and a variety of sample matrices.

The assessment of combustion data, positive identification and quantitation of the selected compounds are dependent on integrity of the samples received and the precision and accuracy of the analytical methods employed. The quality assurance procedures for this method are designed to monitor the performance of the analytical method and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

7.2.1 Field Blanks. The field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, and unused filters and resin cartridges. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area and leak checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train.

7.2.2 Method Blanks. A method blank must be prepared for each set of analytical operations to evaluate contamination and artifacts that can be derived from glassware, reagents and sample handling in the laboratory.

Table 7-1. QUALITY ASSURANCE PROCEDURES FOR TRACE ORGANIC ANALYSIS

Field blanks	1 - Flue gas sampling train per day 10% - Filter returned unused 10% - Resin cartridges returned unused 1 - Field solvent blanks per lot 3 - Sample containers used
Method blanks	1 - Analytical method blank
Method validations	Method procedures studied and validated with spiked blanks and spiked samples prior to initiating analysis program
Surrogate spiking compounds	Dioxane-d_8, pyridine-d_5, toluene-d_8, chlorobenzene-d_5, phenol-d_5, nitrobenzene-d_5, naphthalene-d_8, and pentachlorophenol-$^{13}C_6$ spiked in all samples prior to extraction to provide recovery and precision data. In addition where available labeled analogs of the POHC of interest should be spiked.
Column performance mixture	Grob test mixture to evaluate and identify capillary column characteristics.
Internal standards for quantitation	Phenanthrene-d_{10}
Performance tests	Interlaboratory testing/split samples and/or performance audit samples

7.2.3 Method Performance Evaluation. Evaluation of analytical procedures for a selected series of compounds must include the sample preparation procedures, and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

7.2.4 Capillary Column Performance Tests. Capillary columns will be evaluated and characterized utilizing Grob type mixtures. The columns will be evaluated on installation and at least once per week thereafter. In addition if column performance deteriorates, steps must be taken to improve the performance or the column must be replaced.

7.2.5 Surrogate Spiking Compounds. The number of samples required to establish the precision and accuracy of a method can be significantly reduced by utilizing surrogate compounds as performance indicators. By utilizing stable isotope-labeled compounds, method performance can be monitored on a routine basis without the cost of additional spiked analyses. Stable isotope-labeled compounds that have the same physical and chemical characteristics as the analyte and that are not present in the samples are ideal choices for determining method performance.

The recoveries of the stable isotope labeled surrogate compounds are used as the primary measurement of method analysis precision. In addition, the spiking of surrogate standards in all sample field blanks, method blanks and actual samples prior to extractions can be used to determine whether any sample matrix effects or other analytical problems affect the accuracy of the analyses.

7.3 Quantitative Analysis. Quantitative analytical methods are used to estimate the level of hazardous compounds in various matrices. The process of estimation or quantitation requires the precision, accuracy (bias), and detection limit of the analytical method to be known and documented.

7.3.1 Calibration.

1) Initial calibration standards are to be prepared and analyzed in the concentration series 0 (blank), 0.5X, X, 2X, 5X, and 10X where X is the concentration in the solvent being analyzed corresponding to the required or desired detection limit in the original matrix.

2) Daily Calibration. An instrument calibration standard will be run prior to analyses each day to establish that the sensitivity of the instrument has not changed over the working range. Data generated will be compared against the cumulative data to date to establish the stability of the instrument response.

3) Quality control samples are to be inserted at random in a sample analysis series. At least one control sample is to be included with each lot of samples. The types of control samples are chosen to minimize the number of control samples and maximize the quality control data obtained from the analytical system. For example, a spike of a previously analyzed combustion sample or blank XAD-2® extract containing no detectable analyte may exhibit matrix effects that will not be demonstrated by a spike in a standard solvent.

4) Data generated from daily control samples are to be used to update control charts and, by addition to the existing data base, to refine the detection limit of the analytical method as well as the estimates of precision and accuracy.

5) Concentration values less than the average detection limit of the method will be reported as "less than" the detection limit unless sufficient data exist to justify a lower detection limit. Conversely, detection limits higher than the average detection limit (as is the case of a sample with high background interferences) will be reported as "less than" the higher detection limit.

7.4 Optimization of the GC/FID and GC/MS Procedures. GC operating conditions will be optimized by analyzing solutions containing a variety of the candidate POHCs by the GC/FID technique. The column head pressure is adjusted appropriately to maximize the FID response to the test mixtures. These adjustments are used to select the optimum carrier gas velocity.

Having established GC operating conditions by the GC/FID procedure, the method is then applied to the determination of the candidate POHCs by GC/MS. The mass spectrometer is operated in full scan (40 to 450 amu) in the EI mode. The scan time is maintained at ≦1 s to enable the collection of enough scans to characterize each capillary GC peak.

7.5 GC Quality Control Procedures. The GC/FID and GC/MS procedure will include calibration utilizing standard solutions of the candidate POHCs. Five-point calibration curves are prepared for each candidate POHC determined by gas chromatography. Each response of the FID and/or MS response (relative to phenanthrene-d_{10}) as a function of the quantity of the particular POHC injected on the GC column will be plotted.

In addition to the use of standards for the calibration, the performance of the GC/MS system is checked daily with decafluorotriphenylphosphine (DFTPP) according to the requirements given in EPA Method No. 625. The performance criteria listed in Table 4-2 will be met.

The precision of determinations by GC/FID and GC/MS is assessed by triplicate injections of at least one standard solution of each POHC investigated by gas chromatography. The estimate of precision of the replicate measurements is expressed as the relative standard deviation (RSD) calculated from Equation 1

$$\text{RSD}\ (\%) = \frac{\text{SD}}{\text{X}}\ 100 \tag{1}$$

Standard Deviation (SD) is calculated from Equation 2

$$\text{SD} = \left[\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{(n-1)}\right]^{\frac{1}{2}} \tag{2}$$

Mean relative response ($\bar{X}$) is calculated from Equation 3

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \tag{3}$$

where:

n = Number of replicate measurements.

X_i = Relative response of the POHC standard.

Phenanthrene-d_{10} will be used as an internal standard in all GC methods. Along with the analytes phenanthrene-d_{10} will be injected to minimize the effect of injection volume and instrument performance upon the precision of determinations. Also, the phenanthrene-d_{10} internal standard is used to calculate the relative response factor (RRF) for each POHC from Equation 4.

$$RRF = (A_s C_{is})/(A_{is} C_s) \qquad (4)$$

where:

A_s = Area of the characteristic ion for the POHC to be measured.
A_{is} = Area of the characteristic ion for the internal standard.
C_{is} = Concentration of the internal standard (μg/mL).
C_s = Concentration of the POHC (μg/mL) to be measured.

7.6 Statistical Analysis of Data.

7.6.1 Found Concentration.

1) Instrument calibration standards to cover the range of anticipated concentrations are prepared. These calibration standards are introduced to the instrument to obtain responses for the various concentrations.

2) An instrument calibration curve is constructed by plotting the response versus the calibration standard concentration and determining the best fit regression curve for the data. A measure of the linearity of the responses is the correlation coefficient. The mean of the values obtained will be used instead of a regression if the values agree within 10 percent.

3) The found concentration from the analysis of a sample is obtained by entering the instrument calibration curve with the sample response and reading the corresponding concentration. The concentration read from the calibration curve must be modified to reflect the concentration in the original matrix assuming 100 percent recovery through the analytical method. The resultant concentration is the found concentration.

7.6.2 Detection Limit.

1) Before any analytical system is employed in a determination, sufficient spikes and blanks will be run to statistically establish the lowest concentration which may be distinguished from zero. The lowest calculated concentration will be reported as the detection limit of the method provided that at least one of the spike (target) concentrations is below the calculated detection limit. Otherwise, the lowest spike concentration is the minimum level that can be reported as the detection limit. The highest spike concentration will represent the upper limit of reportable data.

2) The detection limit is derived from the assumption that the relationship between the found concentration and target concentration is linear, and that the variance about the least squares linear regression line is homogeneous over the tested concentration range, and that the distribution of found concentrations for a given target concentration is a normal distribution.

   Based on these assumptions, the least squares linear regression line of the form, $y = y_o + bx$, is determined, where:

   y_o = y axis (found concentration) intercept.
   b = Slope of the line.
   x = Target concentration.

A measure of the linearity of the data is the correlation coefficient. The confidence limits about the regression line are given by:

$$y = yo + bx + s\, t_{(n-2),\ (1-\alpha/2)} \left(\frac{1}{n} + \frac{(x-\bar{x})^2}{\Sigma(x_i-\bar{x})^2} \right)^{\frac{1}{2}}$$

for the upper confidence limit and

$$y = yo + bx - s\, t_{(n-2),\ (1-\alpha/2)} \left(\frac{1}{n} + \frac{(x-\bar{x})^2}{\Sigma(x_i-\bar{x})^2} \right)^{\frac{1}{2}}$$

for the lower confidence limit, where:

$$s = [[\Sigma y^2 i - a\Sigma yi - b\Sigma xiyi]/(n-2)]^{\frac{1}{2}}$$

where:

$t_{(n-2),\ (1-\alpha/2)}$ = Student's t for (n-2) degrees of freedom and a level of significance of α, and

n = total number of data points.

The detection limit, x_d, is the value of x corresponding to a point on the lower confidence limit curve where the value of y equals the value of y on the upper confidence limit curve at x = 0.

7.6.3 Documentation Surrogate (Target) Recoveries. Each sample fraction that is analyzed will be spiked with the following surrogate (see Table 7-2) compounds at 10X where X is the minimum detectable level for the individual compound. In addition where readily available stable labeled analogs of the POHC's being incinerated should be spiked in the indirect fractions at levels based on the following: (1) target detection limits for the selected POHC's and (2) expected concentrations of the organic waste components. For example, incineration effluent samples would require spiking levels of labeled compounds at 2 to 10 times the detection limit required to measure 99.99% DRE of the POHCs.

Data generated will be compiled in Table 7-2 and treated as shown in Table 7-3. Surrogate recovery will be for the total sample, i.e., the average found value for all fractions of a sampling train, and treated for each individual fraction.

Table 7-2. SURROGATE DATA

Surrogate(s)	Target concentration 10X, where X equal MDL	Organic rinse(s) 1	Condensate 2	Impingers 3	XAD_2/ filter 4
Dioxane-d_8	250 μg[a]				
Pyridine-d_5	250 μg				
Toluene-d_8	250 μg				
Chlorobenzene-d_5	250 μg				
Phenol-d_5	250 μg				
Nitrobenzene-d_5	250 μg				
Naphthalene-d_8	250 μg				
Pentachlorophenol-$^{13}C_6$	250 μg				

[a] Total μg based on an assumed MDL of 25 ng on-column;

10 mL concentrate = 25 ng/μL on-column

1 mL concentrate = 250 ng/μL on-column

Table 7-3. SURROGATE RECOVERIES

Surrogate(s)	Target concentration (μg)	Average found value	Standard deviation	Percent imprecision	Percent inaccuracy
Dioxane-d_8	250				
Pyridine-d_5	250				
Toluene-d_8	250				
Chlorobenzene-d_5	250				
Phenol-d_5	250				
Nitrobenzene-d_5	250				
Naphthalene-d_8	250				
Pentachlorophenol-$^{13}C_6$	250				

$$\text{Percent relative standard deviation} = \frac{S}{\bar{X}} \times 100$$

where:

S = Standard deviation.

$\bar{X}$ = Average found concentraton.

$$\text{Percent recovery} = \frac{\bar{X}}{TC} \times 100$$

where:

$\bar{X}$ = Average found concentration of the TC.

TC = Target concentration.

8. References

1. Addendum to Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC, December 6, 1967.

2. Code of Federal Regulations. Title 40, Part 60, Appendix A, Methods 1-5.

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5. Martin, R.M. Construction Details of Isokinetic Source - Sampling Equipment. Research Triangle Park, NC, Environmental Protection Agency, April, 1971. PB-203 060/BE, APTD-0581. 35 pp.

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APPENDIX A-1

CLEANING OF GLASSWARE

In the analysis of samples containing components in the parts per billion range, the preparation of scrupulously clean glassware is mandatory. Failure to do so can lead to a myriad of problems in the interpretation of the final chromatograms due to the presence of extraneous peaks resulting from contamination. Particular care must be taken with glassware such as Soxhlet extractors, Kuderna-Danish evaporative concentrators, sampling train components, or any other glassware coming in contact with an extract that will be evaporated to a lesser volume. The process of concentrating the compounds of interest in this operation may similarly concentrate the contamination substance, resulting in extraneous chromatographic peaks that, in extreme cases, may completely overlap and mask peaks of interest.

Although chemists do not all agree on procedural details in the cleaning of glassware, the majority are in agreement regarding the basic cleaning steps. These are:

1. removal of surface residuals immediately after use;
2. hot soak to loosen and flotate most particulate material;
3. hot water rinse to flush away flotated particulate;
4. soak with oxidizing agent to destroy traces of organic compounds;
5. hot water rinse to flush away materials loosened by deep penetrant soak;
6. distilled water rinse to remove metallic deposits from the tap water; and
7. methanol rinse to flush off any final traces of organic materials and remove the water.

Each of these eight fundamental steps will be discussed in the order in which they appear above.

1. As soon as possible after use of glassware coming in contact with sample, i.e., beakers, pipets, flasks, or bottles used for standards, the glassware should be methanol-flushed before placing in the hot detergent soak. If this is not done, the soak bath may serve to contaminate all other glassware placed therein.

2. The hot soak consists of a bath of a suitable detergent in water of 50°C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard water scum or curd would have an affinity particularly for many chlorinated compounds and, being almost wholly water insoluble, would deposit on all glassware in the bath in a thin film.

   There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form, is manufactured by Alconox, Inc., New York and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

3. No comments required.

4. The most common and highly effective oxidizing agent for removal of traces of organic compounds is the traditional chromic acid solution made up of H_2SO_4 and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40 to 50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves, and apron. The bench area where this operation is conducted should be covered with lead sheeting as spattering will disintegrate the unprotected bench surface.

   The potential hazards of using chromic sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca 0.1 N NaOH upon dilution, and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attack glass nor exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157", manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex", a product of Borer-Chemie, Solothurn, Switzerland.

5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware may pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended as contaminants may be introduced to the interior of the cleaned vessels. Neoprene-coated metal racks are suitable for such items as beakers, flasks, chromatographic tubes, and any glassware then can be inverted and suspended to dry. Small articles like stirring rods, glass stoppers, and bottle caps can be wrapped in aluminum foil and oven-dried a short time if oven space is available. Under no circumstance should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

As an option, the glassware can be heated to a minimum of 300°C to vaporize any organics.

APPENDIX A-2
PREPARATION OF XAD-2® SORBENT RESIN

1. SCOPE AND APPLICATION

XAD-2® resin, as supplied by the manufacturer, is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Both the salt solution and any residual extractable monomer and polymer species must be removed before use. The resin is prepared by a series of water and organic extractions followed by careful drying.

2. EXTRACTION

2.1 Method 1

The procedure may be carried out in a giant Soxhlet extractor. An all-glass thimble containing an extra-coarse frit is used for extraction of XAD-2®. The frit is recessed 10-15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen since it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse - place resin in a beaker and rinse once with D.I. water and discard. Fill with water a second time and let stand overnight and discard.
Water	Extract with H_2O for eight hours.
Methyl alcohol	Extract for 22 hours.
Methylene chloride	Extract for 22 hours.
Methylene chloride (fresh)	Extract for 22 hours.

2.2 Method 2

As an alternative to Soxhlet extraction, a continuous extractor has also been fabricated for the extraction sequence and is described in Figure B-1. This extractor has been found to be acceptable. The particular canister used for the apparatus shown in Figure A-2-1 contains about 500 g of finished XAD-2®. Any size may be constructed; the choice is dependent on the needs of the sampling programs. The XAD-2® is held under light spring tension between a pair of coarse and fine screens. Spacers under the bottom screen allow for even distribution of clean solvent. The three-necked flask should be of sufficient size (3 L in this case) to hold solvent equal to twice the dead volume of the XAD-2® canister. Solvent is refluxed through the Snyder column and the distillate continuously cycled up through the XAD-2® for extraction and returned to the flask. The flow is maintained upwards through the XAD-2® for extraction and returned to the flask. The flow is maintained upwards through the XAD-2® to allow maximum solvent contact and prevent channeling. A valve at the bottom of the canister allows removal of solvent from the canister between changes.

Experience has shown that it is very difficult to cycle sufficient water in this mode. Therefore, the aqueous rinse is accomplished by simply flushing the canister with about 20 L of distilled water. A small pump may be useful for pumping the water through the canister. The water extraction should be carried out at the rate of about 20-40 mL/min.

After draining the water, subsequent methyl alcohol and methylene chloride extractions are carried out using the refluxing apparatus. An overnight or 10- to 20-hour period is normally sufficient for each extraction.

All materials of construction are glass, Teflon®, or stainless steel. Pumps, if used, should not contain extractable materials. Pumps are not used with methanol and methylene chloride.

3. DRYING

After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proven to be the fastest and most reliable drying method.

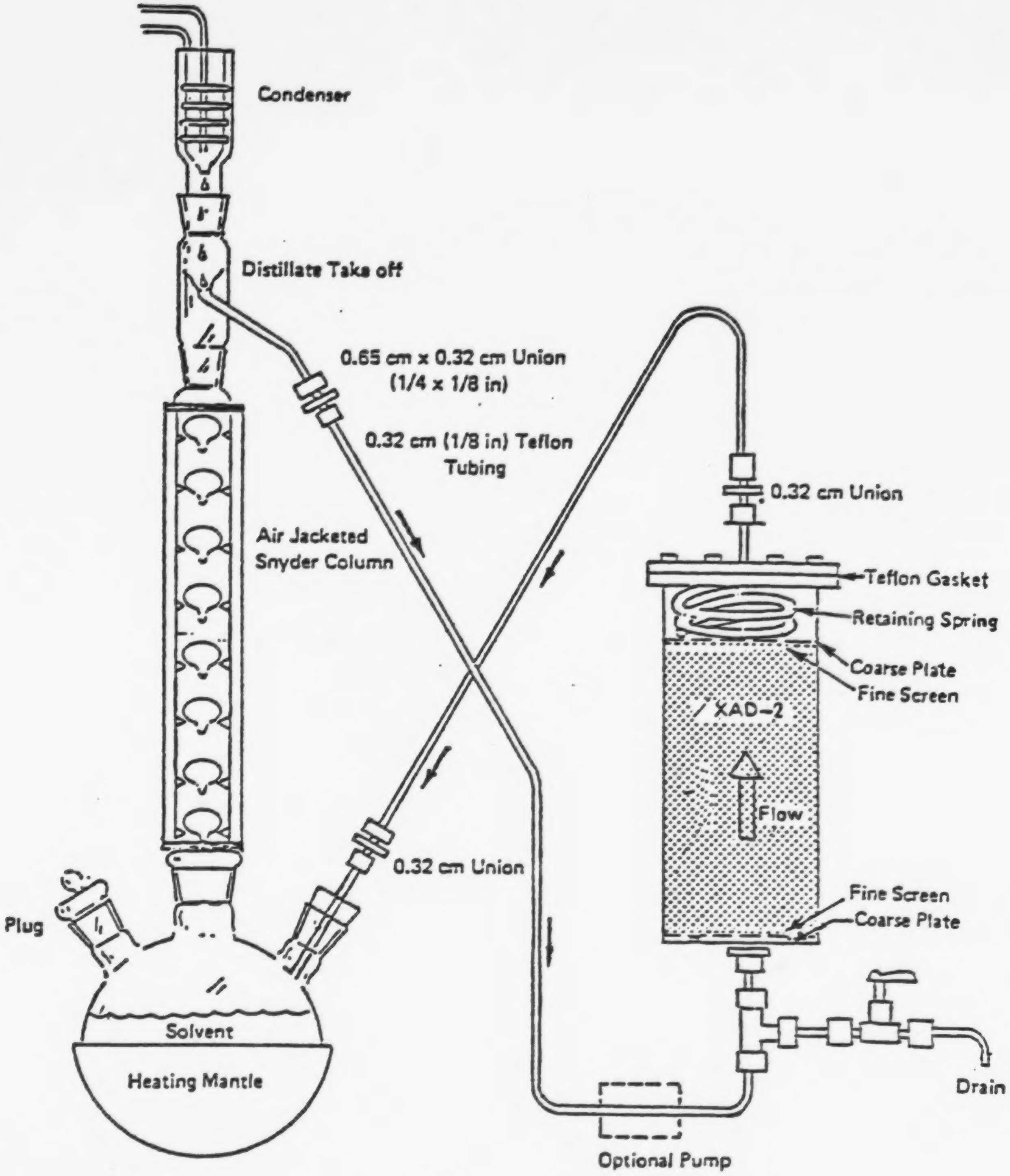
Condenser
Distillate Take off
0.65 cm x 0.32 cm Union
(1/4 x 1/8 in)
0.32 cm (1/8 in) Teflon
Tubing
0.32 cm Union
Air Jacketed
Snyder Column
Teflon Gasket
Retaining Spring
Coarse Plate
Fine Screen
XAD-2
Flow
0.32 cm Union
Fine Screen
Coarse Plate
Plug
Solvent
Heating Mantle
Drain
Optional Pump

Figure A-2-1. XAD-2® cleanup extraction apparatus.

A simple column with suitable retainers as shown in Figure A-2-2 will serve as a satisfactory column. A 10.2-cm (4-in) Pyrex® pipe 0.6 m (2 ft) long will hold all of the XAD-2® from the extractor shown in Figure B-1 or the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum resin load at the exit of the column.

3.1 Method 1

The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2®. Liquid nitrogen from a regular commercial liquid nitrogen cylinder has routinely proven to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95-cm (3/8-in) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2® may be dried overnight consuming a full 160-L cylinder of liquid nitrogen.

3.2 Method 2

As a second choice, high purity tank nitrogen may be used to dry the XAD-2®. The high purity nitrogen must first be passed through a bed of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidization may cause the particles to break up.

4. QUALITY CONTROL PROCEDURES

For both Methods 1 and 2, the quality control results must be reported for the batch. The batch must be re-extracted as discussed in Section 3.2.1 if the residual extractable organics are greater than 20 μg/mL by TCO analysis, or the gravimetric residue is greater than 0.5 mg/20 g XAD-2® extracted.

Four control procedures are used with the final XAD-2® to check for (1) residual methylene chloride, (2) extractable organics (TCO), (3) specific compounds of interest as determined by GC/MS as described in Section 4.4, and (4) residue (GRAV).

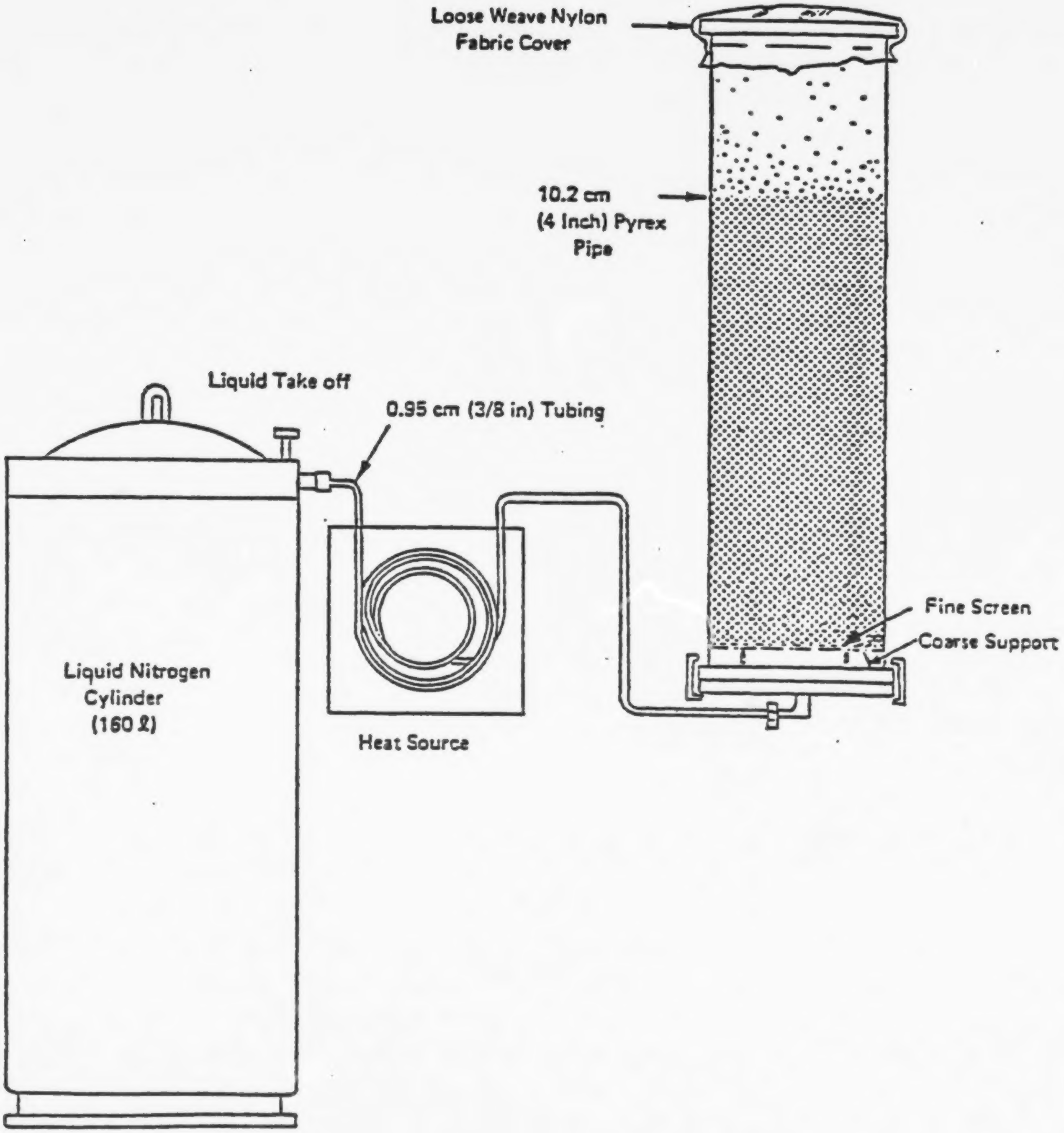
Loose Weave Nylon
Fabric Cover
10.2 cm
(4 Inch) Pyrex
Pipe
Liquid Take off
0.95 cm (3/8 in) Tubing
Fine Screen
Coarse Support
Liquid Nitrogen
Cylinder
(160 ℓ)
Heat Source

Figure A-2-2. XAD-2® fluidized-bed drying apparatus.

4.1 Procedure for Residual Methylene Chloride

4.1.1 Description. A 1 ±0.1 g sample of dried resin is weighed into a small vial, 3 mL of toluene are added, and the vial is capped and well shaken. Five microliters of toluene (now containing extracted methylene chloride) are injected into a gas chromatograph, and the resulting integrated area is compared to a reference standard.

The reference solution consists of 2.5 µL of methylene chloride in 100 mL of toluene, simulating 100 µg residual methylene chloride on the resin. The acceptable maximum content is 1,000 µg/g resin.

4.1.2 Experimental.

- 6 ft x 1/8 in SS column containing 10 percent OV-101 on 100/120 Supelcoport.
- Helium carrier at 30 mL/minute.
- FID operated on 4 x 10^{-11} A/mV.
- Injection port temperature: 250°C.
- Detector temperature: 305°C.
- Programmed: 30°C(4 min) $\underline{40°/min}$ 250°C (hold).
- Program terminated at 1,000 seconds.

4.2 Procedure for Residual Extractable Organics

4.2.1 Description. A 20 ±0.1 g sample of cleaned, dried resin is weighed into a precleaned alundum or cellulose thimble which is plugged with cleaned, glass wool. (Note that 20 g of resin will fill a thimble, and the resin will float out unless well plugged.) The thimble containing the resin is extracted for 24 hours with 200 mL of pesticide-grade methylene chloride.*

The 200-mL extract is reduced in volume to 10 mL using a Kuderna-Danish concentrator and/or a nitrogen evaporation stream. Five microliters of that solution are analyzed by gas chromatography using the TCO analysis procedure. The concentrated solution should not contain more than 20 μg/mL of TCO extracted from the XAD-2®. This is equivalent to 10 μg/g of TCO in the XAD-2® and would correspond to 1.3 mg of TCO in the extract of the 130-g XAD-2® module. Care should be taken to correct the TCO data for a solvent blank prepared (200 → 10 mL concentration) in a similar manner.

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*Burdick and Jackson pesticide grade or equivalent purity.

4.2.2 Experimental. Use the TCO analysis conditions described in the revised Level 1 manual (EPA 600/7-78-201).

4.3 GC/MS Screen

The extract, as prepared in 4.2, is subjected to GC/MS analysis for each of the individual compounds of interest. The GC/MS procedure is described in Section 4.4 of Appendix A. The extract is screened at the MDL of each compound. The presence of any compound at a concentration greater than 25 μg/mL in the concentrated extract will require the XAD-2® to be re-cleaned by repeating the methlyene chloride step.

4.4 Methodology for Residual Gravimetric Determination

After the TCO value and GC/MS data are obtained for the resin batch by the above procedures, dry the remainder of the extract in a tared vessel. There must be less than 0.5 mg residue registered or the batch of resin will have to be extracted with fresh methylene chloride again until it meets this criterion. This level corresponds to 25 μg/g in the XAD-2® or about 3.25 mg in a resin charge of 130 g.

APPENDIX A-3

MS - ANALYTICAL IONS

This appendix lists the Appendix VIII Hazardous Constituents (according to the May 20, 1981 Federal Register) that are analyzed by GC/MS procedures with the appropriate MS analytical ions and their corresponding intensities.

MS - ANALYTICAL IONS

Compound	Ions (Intensities)
Acetonitrile	41(100), 40(50), 39(17), 38(5)
Acetophenone	105(100), 77(83), 51(31), 120(25)
2-Acetylaminofluorene	181(100),180(82), 223(62), 152 (37)
Acrolein	56(72), 27(100), 26(54), 55(51)
Acrylamide	27(100), 44(89), 71(72), 55(58)
Acrylonitrile	53(100), 26(93), 52(79), 51(30)
Aldrin	66(100), 263(73), 220(11)
Allyl alcohol	57(100), 29(39), 31(32), 58(26)
4-Aminobiphenyl	169(100), 170(14), 168(11), 84.5(9)
5-(Aminomethyl)-3-isoxazolol	98(100), 41(66), 39(49), 67(23)
Amitrole	28(100), 84(66), 57(28), 29(23)
Aniline	93(100), 66(33), 65(18), 39(18)
Aramite	
Auramine	
Benz(c)acridine	229(100), 228(19), 230(19), 201(10)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Benz(a)anthracene	228(100), 229(19), 226(19), 114(18)
Benzene	78(100), 77(19), 52(16), 51(15)
Benzene, dichloromethyl-	
Benzenethiol	110(100), 66(38), 39(28), 109(25)
Benzidine	184(100), 185(15), 183(11), 92(8)
Benzo(b)fluoranthene	252(100), 250(25), 253(25), 126(25)
Benzo(j)fluoranthene	252(100), 250(25), 253(25), 126(25)
Benzo(a)pyrene	252(100), 250(25), 253(23), 125(21)
p-Benzoquinone	108 (100), 54(99), 82(37), 53(32)
Benzotrichloride	159(100), 161(64), 89(14), 163(11)
Benzyl chloride	91(100), 126(28), 65(9), 92(8)
Bis(2-chloroethoxy)methane	93(100), 63(65), 95(32), 27(22)
Bis(2-chloroethyl) ether	93(100), 63(98), 27(75), 95(32)
N,N-Bis(2-chloroethyl)-2-naphthylamine	
Bis(2-chloroisopropyl) ether	45(100), 43(36), 41(34), 77(19),
Bis(chloromethyl)ether	79(100), 49(47), 81(33), 51(16)
Bis(2-ethylhexyl) phthalate	149(100), 57(54), 169(33), 71(27)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Bromoacetone	43(100), 15(84), 14(19), 79(13)
Bromomethane	94(100), 96(94), 15(47), 93(21)
4-Bromophenyl phenyl ether	248(100), 250(99), 141(45), 77(32)
Brucine	
2-Butanone peroxide	
Butyl benzyl phthalate	149(100), 91(50), 206(18), 104(12)
2-sec-Butyl-4,6-dinitrophenol (DNBP)	
Carbon disulfide	76(100), 32(22), 44(17), 78(9)
Carbon oxyfluoride	47(100), 66(55), 28(14), 31(4)
Chloral	*
Chlordane (alpha and gamma isomers)	373(19), 375(17), 377(10)
Chlorinated benzenes, N.O.S.	112(100), 77(45), 114(33), 51(12)
Chlorinated ethane, N.O.S.	64(100), 28(91), 29(84)
Chlorinated fluorocarbons, N.O.S.	**
Chlorinated naphthelene, N.O.S.	162(100), 164(33), 127(30)
Chlorinated phenol, N.O.S.	128(100), 130(33), 65(24)
Chloroacetaldehyde	*
Chloroalkyl ethers	**
p-Chloroaniline	127(100), 65(34), 129(31), 92(20)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensitites)
Chlorobenzene	112(100), 77(45), 114(33), 51(12)
Chlorobenzilate	
p-Chloro-m-cresol	142(100), 107(80), 144(32), 77(24)
1-Chloro-2,3-epoxypropane	
2-Chloroethyl vinyl ether	63(100), 27(62), 43(42), 44(38)
Chloroform	83(100), 85(64), 47(37), 35(20)
Chloromethane	50(100), 52(32), 15(21), 49(9)
Chloromethyl methyl ether	45(100), 29(25), 15(22), 49(17)
2-Chloronaphthalene	162(100), 164(33), 127(33), 128(17)
2-Chlorophenol	128(100), 130(33), 65(24), 64(12)
3-Chloropropionitrile	49(100). 54(77). 51(39). 53(26)
Chrysene	228(100), 226(26), 229(21), 114(13)
Coal Tars	**
Creosote	**
Cresols	**
Crotonaldehyde	*
2-Cyclohexyl-4,6-dinitrophenol	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
DDD	235(100), 237(66), 165(38), 75(21)
DDE	246(100), 318(83), 316(66). 248(58)
DDT	235(100), 237(72), 165(59),75(22)
Diallate	
Dibenz(a,h)acridine	279(100), 280(25), 139.5(23), 278(14)
Dibenz(a,j)acridine	279(100), 280(25), 139.5(23), 278(14)
Dibenz(a,h)anthracene	278(100), 139(24), 279(16), 276(16)
7H-Dibenzo(c,g)carbazole	
Dibenzo(a,e)pyrene	302(100)
Dibenzo(a,h)pyrene	302(100)
Dibenzo(a,i)pyrene	302(100)
1,2-Dibromo-3-chloropropane	157(100), 155(78), 75(46), 159(25)
1,2-Dibromomethane	107(100), 109(95), 27(54), 28(11)
Dibromoethane	174(100), 93(72), 95(62), 172(52)
Di-n-butyl phthalate	149(100), 41(28), 29(25), 28(22),
Dichlorobenzene (meta, ortho and para isomers)	146(100) 148(62), 111(39), 75(23)
Dichlorobenzene, N.O.S.	146(100), 148(62), 111(39), 75(23)
3,3'-Dichlorobenzidine	252(100), 254(67), 256(10), 126(12)
1,4-Dichloro-2-butene	75(100), 89(48), 53(36), 77(33)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Dichlorodifluoromethane	
1,1-Dichloroethane	63(100), 27(72), 65(33), 83(12)
1,2-Dichloroethane	62(100), 64(33), 27(70)
trans-1,2-Dichloroethene	61(100), 96(80), 98(51), 63(29)
Dichloroethylene, N.O.S.	146(100), 148(62), 111(38), 113(13)
1,1-Dichloroethylene	61(100), 96(80), 98(52), 63(33)
Dichloromethane	49(100), 84(72), 86(44), 51(31)
2,4-Dichlorophenol	162(100), 164(65), 63(65), 98(40)
2,6-Dichlorophenol	162(100), 164(64), 63(29), 126(20),
2,4-Dichlorophenoxyacetic acid (2,4-D)	162(100), 220(78), 164(64), 222(49)
Dichloropropane, N.O.S.	63(100), 62(74), 27(41), 41(34)
1,2-Dichloropropane	79(100), 81(38), 43(27), 49(20)
Dichloropropanol, N.O.S.	
Dichloropropene, N.O.S.	75(100), 77(33), 110(25), 112(15)
1,3-Dichloropropene	75(100), 39(55), 77(32), 49(26)
Dieldrin	79(100), 108(19), 263(18), 277(18)
1,2:3,4-Diepoxybutane	55(100), 44(91), 43(73), 29(65)
N,N-Diethylhydrazine	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
0,0-Diethyl S-methyl ester of phosphordithioic acid	
0,0-Diethylphosphoric acid, O-p-nitrophenyl ester	
Diethyl phthalate	149(100), 177(28), 150(13), 176(9)
0,0-Diethyl O-2-pyrazinyl phosphorothioate	
Dihydrosafrole	163(100), 164(25), 77(19), 51(12)
Diisopropylfluorophosphate	
Dimethoate	
3,3'-Dimethoxybenzidine	244(100), 184(61), 201(38), 229(21)
p-Dimethylaminoazobenzene	120(100), 225(73), 77(58), 42(38)
7,12-Dimethylbenz(a)anthracene	256(100), 241(70), 257(48), 240(46)
3,3'-Dimethylbenzidine	
1,1-Dimethylhydrazine	60(100), 42(51), 59(45), 45(42)
1,2-Dimethylhydrazine	60(100), 42(98), 28(53), 45(52)
alpha,alpha-Dimethylphenethylamine	58(100), 91(7), 59(5), 134(3)
2,4-Dimethylphenol	122(100), 107(90), 121(55), 91(20)
Dimethyl phthalate	163(100), 77(19), 164(10), 194(6)
Dimethyl sulfate	15(100), 29(71), 95(66), 31(66)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Dinitrobenzene, N.O.S.	30(100), 75(75), 168(70), 76(52)
4,6-Dinitro-o-cresol and salts	
2,4-Dinitrophenol	
2,4-Dinitrotoluene	165(100), 89(65), 90(26), 63(35)
2,6-Dinitrotoluene	165(100), 89(52), 90(35), 148(22)
Di-n-octyl phthalate	149(100), 57(39), 167(32), 279(2)
1,4-Dioxane	28(100), 29(32), 59(24), 88(22)
Diphenylamine	
1,2-Diphenylhydrazine	77(100), 182(29), 105(23), 93(15)
Di-n-propylnitrosamine	70(100), 42(99), 117(79), 43(65)
Disulfoton	
2,4-Dithiobiuret	
Endosulfan	201(100), 283(48), 278(30)
Endrin and metabolites	81(100), 263(70), 82(61)
Ethyl carbamate	
Ethyleneimine	42(100), 43(62), 28(59), 15(22)
Ethyl methacrylate	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Ethyl methansulfonate	79(100), 109(78), 97(26), 80(19)
Fluoroanthene	202(100), 200(20), 203(18), 101(13)
Fluoroacetic acid, sodium and salt	
Formaldehyde	*
Formic acid	
Glycidylaldehyde	*
Halomethane, N.O.S.	**
Heptachlor	100(100), 272(60), 274(46)
Heptachlor epoxide (alpha, beta and gamma isomers)	355(100), 353(79), 351(60)
Hexachlorobenzene	284(100), 286(80), 282(53), 142(29)
Hexachlorobutadiene	225(100), 227(65), 223(63), 260(38)
Hexachlorocyclohexane (all isomers)	181(100), 183(99), 109(80), 217(78)
Hexachlorocyclopentadiene	
Hexachloroethane	117(100), 119(95), 199(50), 201(85)
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo, endo-dimethanonaphthalene	
Hexachlorophene	
Hexachloropropene	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Hexaethyl tetraphosphate	
Hydrazine	32(100), 31(47), 29(40), 30(31)
Indeno(1,2,3-c,d)pyrene	276(100), 138(38), 277(26), 274(21)
Iodomethane	142(100), 127(38), 141(14), 15(13)
Isocyanic acid, methyl ester	
Isobutyl alcohol	
Isosafrole	162(100), 104(42), 131(30), 103(28)
Kepone	
Maleic anhydride	26(100), 54(62), 25(61), 28(36)
Maleic hydrazide	
Malononitrile	66(100), 38(34), 39(34), 28(31)
Methyacrylonitrile	
Methanethiol	
Methapyrilene	58(100), 97(71), 72(22), 71(19)
Methoxychlor	
2-Methylaziridine	28(100), 56(80), 57(54), 30(37)
3-Methylcholanthrene	256(100)
4,4'-Methylenebis-(2-chloroaniline)	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Methyl ethyl ketone (MEK)	43(100), 29(24), 72(17), 27(16)
Methyl hydrazine	46(100), 45(61), 28(58), 31(41)
2-Methyllactonitrile	
Methyl methacrylate	41(100), 69(83), 100(51), 39(36)
Methyl methanesulfate	
N-Methyl-N'-nitro-N-nitrosoquanidine	
Methyl parathion	
Methylthiouracil	
Naphthalene	128(100), 127(20), 129(18), 64(7)
1,4-Naphthoquinone	158(100), 104(39), 76(34), 102(31)
1-Naphthylamine	143(100), 115(45), 116(25), 144(14)
2-Naphthylamine	143(100), 115(38), 144(14), 116(13)
Nicotine and salts	84(100), 133(27), 42(20), 162(19)
p-Nitroaniline	138(100), 92(50), 108(33), 65(30)
Nitrobenzene	77(100), 128(55), 51(55), 65(25)
Nitroglycerine	46(100), 30(24) 29(15), 76(9)
4-Nitrophenol	65(100), 139(90), 109(72), 81(33)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Nitrosamine, N.O.S.	**
N-Nitrosodi-n-butylamine	84(100), 57(79), 29(53), 41(52)
N-Nitrosodiethanolamine	
N-Nitrosodiethylamine	43(100), 42(68), 44(60), 56(56)
N-Nitrosodimethylamine	74(100), 42(75), 43(40), 44(10)
N-Nitroso-N-ethylurea	
N-Nitrosomethylethylamine	88(100), 42(93), 43(46), 56(24)
N-Nitroso-N-methylurea	
N-Nitroso-N-methylurethane	43(100), 96(76), 66(28), 79(20)
N-Nitrosomethylvinylamine	
N-Nitrosomorpholine	56(100), 116(55), 86(37), 28(13)
N-Nitrosonornicotine	
N-Nitrosopiperidine	42(100), 114(91), 55(56), 56(24)
N-Nitrosopyrrolidine	100(100), 41(61), 42(58), 68(16)
N-Nitrososarcosine	
5-Nitro-o-toluidine	
Octamethylpyrophosphormide	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid	
Paraldehyde	*
Parathion	
Pentachlorobenzene	250(100), 252(62), 248(62), 108(41)
Pentachloroethane	117(100), 119(96), 167(95), 95(93)
Pentachloronitrobenzene (PCNB)	
Pentachlorophenol	266(100), 264(62), 268(63), 165(54)
Phenol	94(100), 66(19), 65(17)
Phenylenediamine	
Phosphorodithioic acid, 0,0-diethyl S-((ethylthio) methyl)ester [Phorate]	
Phosphorothioic acid, 0,0-dimethyl 0-(p-((dimethylamino)sulfonyl)phenyl)ester [Famphur]	
Phthalic acid esters, N.O.S.	**
Phthalic anhydride	104(100), 76(84), 50(40), 148(39)
2-Picoline	
Polychlorinated biphenyl, N.O.S.	**
Pronamide	
1,3-Propane sultone	
n-Propylamine	
Propylthiouracil	

MS ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
2-Propyn-1-ol	55(100), 39(8), 28(6), 29(5)
Pyridine	79(100), 52(71), 51(36), 50(26)
Resorcinol	
Saccharin and salts	183(100), 76(99), 50(72), 120(40)
Safrole	162(100), 131(38), 104(31), 135(26)
1,2,4,5-Tetrachlorobenzene	216(100), 214(79), 218(49), 179(15)
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	322( ), 320( )
Tetrachloroethane, N.O.S.	
1,1,1,2-Tetrachloroethane	83(100), 85(66), 131(7), 133(7)
1,1,2,2-Tetrachloroethane	131( ), 133( ), 117( ), 119( )
Tetrachloroethene	166(100), 164(78), 129(64), 131(62)
Tetrachloromethane	
2,3,4,6-Tetrachlorophenol	
Tetraethyldithiopyrophosphate	
Tetraethylpyrophosphate	
Tetranitromethane	
Toluene	92(65), 91(100), 65(12), 51(6)

MS ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Toluenediamine	121(100), 122(93), 94(17), 105(13)
Toluene diisocyanate	174(100), 145(40), 28(39), 27(38)
Toxaphene	231( ), 233( ), 235( )
Tribromomethane	173(100), 171(50), 175(49), 93(22)
1,2,4-Trichlorobenzene	180(100), 182(95), 184(30), 145(30)
1,1,1-Trichloroethane	97(100), 99(66), 117(17), 119(16)
1,1,2-Trichloroethane	97(100), 83(95), 99(66), 85(60)
Trichloroethene	95(100), 130(90), 132(85), 97(66)
Trichloromethanethiol	
Trichloromonofluoromethane	
2,4,5-Trichlorophenol	196(100), 198(97), 200(31), 97(20)
2,4,6-Trichlorophenol	196(100), 198(96), 200(31), 132(28)
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP or Silvex)	
Trichloropropane, N.O.S.	**
1,2,3,-Trichloropropane	75(100), 39(58), 49(42), 110(37)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
O,O,O-Triethyl phosphorothioate	
sym-Trinitrobenzene	
Tris(2,3-dibromopropyl)phosphate	
Vinyl Chloride	62(100), 27(64), 64(33), 26(18)

N.O.S. = not otherwise specified

*Mass spectrum for aldehydes depends upon derivatization method

**Mass spectrum depends on specific compound

APPENDIX B
GENERATOR EXPERIMENTS AND DATA

The study of the sampling and analysis procedures of the Semi-VOST method was divided into two parts: sample generation studies presented here and laboratory analytical studies which are presented in Appendix D.

OBJECTIVE

The objective of the sample generation studies was to determine the effect of sampling conditions and flue gas composition on the amount of hydrocarbons recovered from the sampling train. Variables which were considered to potentially affect method performance included:

- moisture,
- sulfur dioxide,
- hydrochloric acid,
- oxides of nitrogen,
- sample volume,
- sampling flow rate, and
- hydrocarbon or POHC concentration.

APPROACH

The first task in this study was to select a set of test compounds which would be representative of principal organic hazardous constituents (POHCs). The criteria for compound selection included: (1) incinerability, (2) solubility in water, (3) boiling point, and (4) chemical functionality.

With these criteria in mind, a series of 12 compounds was selected for study which included a range of boiling points from 102°C (1,4-dioxane) to 310°C (pentachlorophenol). Initial experiments were conducted to determine the minimum detection limit (MDL) for each of the 12 compounds combined into a single solution. The analyses were performed using GC/MS. The MDL values and boiling points for these compounds are presented in Table B-1.

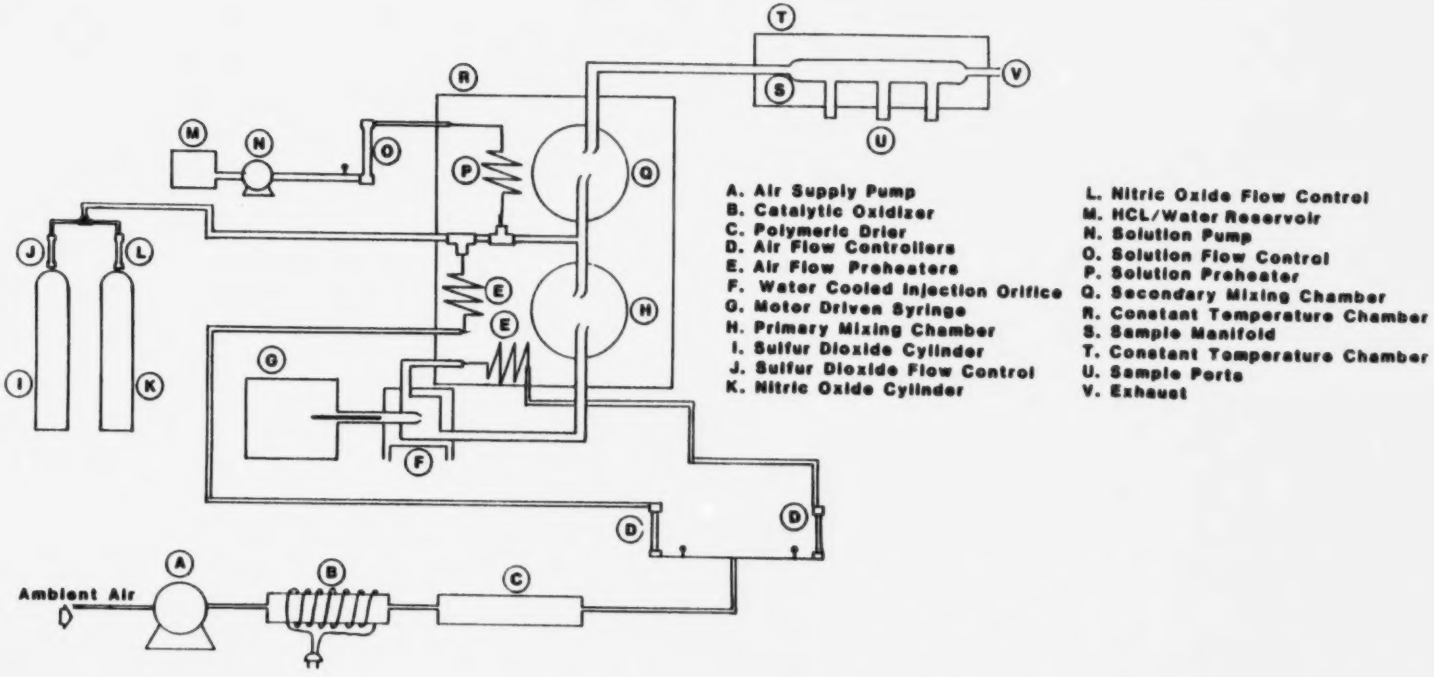
A flue gas simulator was then designed and constructed to evaluate the performance of the method in the laboratory. The simulator, illustrated in Figure B-1, was sized to deliver sufficient "stack" gas volume flows to be sampled simultaneously by two Semi-VOST trains through a heated glass manifold. A hydrocarbon-free air sample stream of approximately 0.6 dscm/min was provided by pumping ambient air through a high temperature catalytic oxidizer and a Perma-Pure® polymeric drier. The air stream was then split with half of the total flow heated to approximately 250°C before introduction of POHCs. Solutions of the test compounds were prepared in methanol and introduced into the hot air stream through a 5-mL motor-driven syringe. Typical solution delivery rates ranged between 20-30 µL/min. The air containing POHCs was then re-heated through a glass mixing bulb before introduction of water, HCl, SO_2, NO_x, and the other half of the clean air stream. Sulfur dioxide and NO_x were introduced from cylinder gas mixtures. HCl was introduced by acidifying the water being metered into the air mixture. The "stack" gas then passed through a second, heated, mixing bulb before entering a glass sampling manifold heated to approximately 300°C. The design parameters provided for 20 percent maximum flue gas moisture levels.

Table B-2 presents a listing of sample generation variables addressed in the study. Table B-3 outlines the test matrix conditions which were based upon a one-half replicate of a 2^5 factorial experimental design. The operating conditions are listed in terms of (1), ab, cd, ae, abcd, etc., as given in the design. The symbol "1" represents Level I of all five independent operating variables. Symbol "ab" represented Level II of Variable A and Variable B, and Level I for Variables C, D, and E.

The draft method formulation was initially followed for both the sampling and analysis of the recovered samples. However, the train rinsing procedure and subsequent sample work-up procedure were modified as now presented in Appendix A.

TABLE B-1. MINIMUM DETECTION LIMIT (MDL)
FOR GC/MS ANALYSIS OF TEST COMPOUNDS OF METHANOL

Selection criteria	Test compound	Boiling point, °C	MDL ng/uL
Incinerability	1,1,2,2-Tetrachloroethane	146	0.25
	Pentachlorophenol	310	4.2
	Hexachloroethane	(sublimes)	0.90
Water solubility	Urethane	180	10.1
	Pyridine	115	8.5
	1,4-Dioxane	102	7.0
Boiling point	Naphthalene	218	0.32
	Chlorobenzene	132	0.37
	Toluene	110	1.9
Chemical functionality	Phenol	182	5.0
	Nitrobenzene	211	1.1
	Resorcinol	280	7.3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Ambient Air
A
B
C
A. Air Supply Pump
B. Catalytic Oxidizer
C. Polymeric Drier
D. Air Flow Controllers
E. Air Flow Preheaters
F. Water Cooled Injection Orifice
G. Motor Driven Syringe
H. Primary Mixing Chamber
I. Sulfur Dioxide Cylinder
J. Sulfur Dioxide Flow Control
K. Nitric Oxide Cylinder
L. Nitric Oxide Flow Control
M. HCL/Water Reservoir
N. Solution Pump
O. Solution Flow Control
P. Solution Preheater
Q. Secondary Mixing Chamber
R. Constant Temperature Chamber
S. Sample Manifold
T. Constant Temperature Chamber
U. Sample Ports
V. Exhaust

Figure B-1. Flue gas simulation system.

TABLE B-2. SAMPLE GENERATION VARIABLES

Variable	Level I	Level II
A	Low moisture High SO_2 (~750 ppmv) High HCl (~1,000 ppmv)	High moisture Low SO_2 (~50 ppmv) Low HCl (~50 ppmv)
B	Low NO_x (~250 ppmv)	High NO_x (~1,000 ppmv)
C	Low hydrocarbon concentration (~3 MDL)	High hydrocarbon concentration (~10 MDL)
D	Small sample size (~0.6 m^3)	Large sample size (~14 m^3)
E	Low sample flow rate (~0.0028 dscm/min)	High sample flow rate (~0.021 dscm/min)

TABLE B-3. OPERATING LEVELS FOR A 1/2 REPLICATE OF A 2^5 FACTORIAL EXPERIMENT*,†

Block 1	Block 2
(1)	ac
ab	bc
cd	ad
ae	bd
be	ce
abcd	de
acde	abce
bcde	abde

* Reference. Cochran, William G. and Gertrude M. Cox, "Expeimental Designs" Second Edition, John Wiley and Sons, Inc., New York, 1957.

† Block 1 experimental conditions were run on one Semi-VOST train and Block 2 conditions were run on a second Semi-VOST train.

With the proposed design it was possible to determine all the main effects, A, B, C, D, and E, and the two-factor interaction terms, AB, BC, CD, etc. The latter gave some indication of the independence of the main factors. The response (dependent) variable in each case was the amount of hydrocarbon extracted from the XAD-2® resin.

The proposed design given in Table B-3 confounds the CD interaction (which is also the ABE interaction) with Blocks 1 and 2. This design was selected so that the sets of runs indicated for each block could be run on two separate sample trains. It was assumed *a priori* that the CD interaction should be negligible because of the nature of Variables C and D. Doubling the inlet composition of the material entering the bed should double the amount recovered from the bed. Doubling the sample size should also double the amount recovered from the bed. Doubling both the composition and the sample size should quadruple the amount recovered from the bed. This assumption also implies that the XAD-2® resin bed is not saturated with hydrocarbon, i.e., there is no breakthrough.

RESULTS

A summary of the results for the flue gas generator studies is given in Table B-4 in which the data are expressed as percent recovery. Runs 1 and 2 were initial experiments in which only the test compounds were added at the 10 MDL level to a clean air stream and sampled by two Semi-VOST trains "A" and "B." These tests were used to provide an indication of the baseline error for the analysis of subsequent results. The remainder of the tests were carried out by collecting samples with a single train over the range of test conditions. Table B-5 gives the distribution of each compound within a given train as a percentage of the total amount recovered.

TABLE B-4. GENERATOR STUDY, SUMMARY PERCENTAGE RECOVERIES

	Run 1		Run 2		Operating conditions															
	A	B	A	B	(1)	ab	cd	ae	be	abcd	acde	bcde	ac	bc	ad	bd	ce	de	abce	abde
Dioxane	105	83	71	103	100	78	104	112	87	89	133	87	115	67	111	105	114	109	115	101
Pyridine	51	41	31	63	10	41	73	61	14	56	105	88	103	9	69	52	156	27	35	91
Toluene	80	68	82	95	84	84	72	86	75	74	161	93	68	73	117	119	71	141	75	112
Urethane	65	61	74	121*	81	40	48	60	15	32	65	67	67	4	58	38	99	26	59	33
Chlorobenzene	87	71	79	101	90	94	98	107	82	97	123	101	88	85	109	113	93	93	95	110
1,1,2,2-tetra-chloroethane	95	71	84	94	98	105	109	109	86	100	141	113	98	87	99	117	105	104	99	121
Phenol	79	99	77	93	100	71	81	108	66	66	113	105	92	77	81	77	111	86	94	64
Nitrobenzene	85	79	82	101	100	110	107	119	97	106	116	116	108	98	110	131	112	119	110	121
Hexachloroethane	84	80	83	91	100	99	99	117	93	104	104	115	98	101	92	107	101	112	112	102
Naphthalene	92	91	90	99	110	95	100	112	102	100	119	119	95	110	91	110	97	135	101	111
Resorcinol	0	0	0	0	0	0	0	0	23	0	0	1	11	0	0	0	10	0	0	0
Pentachlorophenol	0	0	0	0	0	83	226	169	77	177	0	201	136	22.5	121	120	182	633	219	0

* Suspected outlier.

TABLE B-5. DISTRIBUTION OF COMPOUNDS WITHIN THE SAMPLING TRAIN, PERCENT OF TOTAL COLLECTED

	Dioxane	Pyridine	Toluene	Urethane	Chloro-benzene	1,1,2,2-tetra-chloroethane	Phenol	Nitro-benzene	Hexachloro-ethane	Naphtha-lene	Resorcinol	Pentachloro-phenol
Run 1 Train A												
Rinse	5.9	10.3	.6	ND*	<.1	<.1	2.0	ND	ND	1.0	ND	ND
Condensate	N O	S A M P L E*										N O S A M P L E
XAD	94	89.6	98	100	99.8	99.9	97.9	100	100	99	ND	ND
Impinger	ND	<.1	1.1	ND	<.1	ND	ND	ND	ND	ND	ND	ND
Run 1 Train B												
Rinse	ND	25.6	ND	ND	ND	ND	4.8	0.1	ND	ND	ND	ND
Condensate	N O	S A M P L E										N O S A M P L E
XAD	100	74.4	99.7	100	99.9	100	95.3	99.9	100	99.7	100	ND
Impinger	ND	ND	0.3	ND	.1	ND	ND	ND	ND	.3	ND	ND
Run 2 Train A												
Rinse	ND	ND	ND	ND	ND	.2	.2	ND	ND	27.1	ND	ND
Condensate	N O	S A M P L E										N O S A M P L E
XAD	100	100	99.1	100	99.9	99.8	99.8	100	100	73	ND	ND
Impinger	ND	ND	.9	ND	.1	ND	ND	ND	ND	ND	ND	ND
Run 2 Train B												
Rinse	5.8	8.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Condensate	N O	S A M P L E										N O S A M P L E
XAD	94.2	91.7	100	100	99.9	100	100	100	100	100	ND	ND
Impinger	ND	ND	ND	ND	<.1	ND	ND	ND	ND	ND	ND	
bc Train A												
Rinse	8.2	4	10.9	ND	ND	1.1	58	2.6	ND	3	ND	90.2
Condensate	N O	S A M P L E										N O S A M P L E
XAD	89.6	96	89	100	100	98.9	42	97.4	100	97	ND	9.9
Impinger	2.4	ND	.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
be Train B												
Rinse		75.6	ND	61	.8	2.6	26.2	11	3.5	17.4	100	ND
Condensate	N O	S A M P L E										N O S A M P L E
XAD	79.9	22.4	99.7	39	99.2	97	38.7	89	96.5	82.6	ND	100
Impinger	20	2.1	.3	ND	ND	.3	35.1	ND	ND	ND	ND	ND

(continued)

Table B-5. (continued)

	Dioxane	Pyridine	Toluene	Urethane	Chloro-benzene	1,1,2,2-tetra-chloroethane	Phenol	Nitro-benzene	Hexachloro-ethane	Naphtha-lene	Resorcinol	Pentachloro-phenol
de Train A												
Rinse	ND	ND	13	ND	ND	ND	ND	.4	.3	7.6	ND	ND
Condensate	19.7	92.4	.1	100	ND	1.4	68.4	ND	ND	ND	ND	ND
XAD	76.9	7.6	86.5	ND	100	98.6	31.5	99.6	99.7	92.5	ND	100
Impinger	3.5	ND	.3	ND	ND	ND	ND	ND	ND	ND	ND	ND
(1) Train B												
Rinse	ND	94	ND	ND	ND	2	ND	ND	ND	4.3	ND	ND
Condensate	NO SAMPLE											
XAD	100	6	99.7	100	100	98	100	100	100	95.7	ND	ND
Impinger	ND	ND	.3	ND	ND	ND	ND	ND	ND	ND	ND	ND
ac Train A												
Rinse	4.6	16.9	.5	11	ND	ND	7.4	.3	ND	<.1	ND	29
Condensate	NO SAMPLE											
XAD	80.5	32.7	96.6	32.9	99.8	99	56.9	99.1	100	98.9	100	69.8
Impinger	15.1	50.4	.8	56.1	.2	1	35.8	.2	ND	<.1	ND	.9
acde Train B												
Rinse	6.2	<.1	.4	.6	ND	.3	.5	<.1	ND	ND	ND	ND
Condensate	35.5	87.6	.2	90	ND	ND	74.8	1.4	ND	<.1	ND	ND
XAD	47.1	ND	99.1	ND	99.9	99.7	14.3	98.6	100	99.9	ND	
Impinger	11.2	12.2	.3	9.5	<.1	ND	10.5	ND	ND	ND	ND	ND
ab Train B												
Rinse	4.8	20.5	.6	4.2	ND	ND	4.3	.2	ND	<.1	ND	16.9
Condensate	NO SAMPLE											
XAD	81.1	10.8	98.4	30.4	99.5	97.2	75.5	99.6	100	99.7	ND	83.1
Impinger	14.1	68.7	.9	65.5	.5	2.8	20.2	.3	ND	.2	ND	ND
ad Train A												
Rinse	NA†	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Condensate	41.3	94	.3	86.2	ND	ND	24.1	ND	ND	ND	ND	ND
XAD	44.2	4.8	99.5	12.9	100	100	75.9	100	100	100	ND	100
Impinger	14.6	1.1	.1	.8	ND	ND	ND	ND	ND	ND	ND	ND

(continued)

Table B-5. (continued)

	Dioxane	Pyridine	Toluene	Urethane	Chloro-benzene	1,1,2,2-tetra-chloroethane	Phenol	Nitro-benzene	Hexachloro-ethane	Naphtha-lene	Resorcinol	Pentachloro-phenol
bcde Train A												
Rinse	.8	<.1	1.7	.5	.3	.2	.8	.2	.3	.5	5.3	65.7
Condensate	46	99.1	<.1	96.1	<.1	.1	81.7	2.5	ND	<.1	44.5	2.5
XAD	49.5	.7	98.3	3.3	99.6	99.7	.2	97.2	99.7	99.5	50.2	31.8
Impinger	3.8	.2	<.1	.2	<.1	<.1	.2	<.1	<.1	<.1	ND	<.1
ae Train B												
Rinse	4.4	31.4	.9	6.2	<.1	ND	3.2	.5	ND	.2	ND	44.2
Condensate	NO SAMPLE											
XAD	33.1	5.6	98.5	7.7	99.8	99.5	15	96.4	100	99.7	ND	55.8
Impinger	62.5	63	.5	86.1	.2	.5	81.8	3.1	ND	.1	ND	ND
abce Train A												
Rinse	7.4	36	.5	5.7	ND	1.4	3.3	.4	ND	<.1	ND	42.3
Condensate	NO SAMPLE											
XAD	31.1	1.8	98.3	4.6	99	96.3	11.3	90.1	99.9	99.7	ND	54.4
Impinger	61.5	62.2	1.3	89.8	.6	2.3	85.2	10.1	<.1	.3	ND	3.4
ce Train A												
Rinse	7.8	5.3	.6	3.2	<.1	ND	2.2	.2	ND	<.1	8.5	48.2
Condensate	NO SAMPLE											
XAD	56.5	7.3	98.8	35.7	99.9	98.8	79	99.8	100	99.9	91.5	51.7
Impinger	35.7	87.6	.5	61.1	.1	1.2	19.1	<1	ND	<.1	ND	ND
bd Train A												
Rinse	3.5	11.2	.7	66.5	ND	ND	1.4	ND	ND	ND	ND	ND
Condensate	16.2	56	.2	28.5	ND	ND	15.2	ND	ND	ND	ND	ND
XAD	71.1	21.1	98.7	3.3	99.8	99.7	82.4	100	100	99.9	ND	100
Impinger	9.2	11.5	.5	1.6	.2	.3	.9	ND	ND	<.1	ND	ND
abcd Train B												
Rinse	2.4	11.7	.4	ND	<.1	.4	.2	<.1	ND	<.1	ND	ND
Condensate	22.6	78.5	.2	80	ND	.2	17.8	.2	ND	<.1	ND	ND
XAD	67.4	9.2	98.8	20	99.9	99.2	82	99.8	100	99.9	ND	100
Impinger	9.1	.7	.6	ND	<.1	.2	ND	<.1	ND	<.1	ND	ND

(continued)

Table B-5. (continued)

	Dioxane	Pyridine	Toluene	Urethane	Chloro-benzene	1,1,2,2-tetra-chloroethane	Phenol	Nitro-benzene	Hexachloro-ethane	Naphtha-lene	Resorcinol	Pentachloro-phenol
cd Train B												
Rinse	2.2	2.9	.7	ND	.1	<.1	1	<.1	ND	<.1	ND	6.7
Condensate	30	90.9	.1	92	ND	<.1	61.2	<.1	ND	ND	ND	ND
XAD	52.1	2.6	98.6	6.8	99.6	99.1	34.4	99.1	99.9	99.8	ND	93.4
Impinger	16	3.6	.6	1.3	.3	1.8	3.5	.4	.1	.3	ND	ND
abde Train A												
Rinse	9.8	.6	1.3	ND	.1	4.1	3.2	.5	ND	.2	ND	ND
Condensate	46	91.7	.5	92	ND	.2	79	2.1	ND	<.1	ND	ND
XAD	33.5	7.7	96.9	8	99.2	95	17.8	97.1	100	99.5	ND	ND
Impinger	11	ND	1.4	ND	.8	.7	ND	.3	ND	.3	ND	ND

* No water was collected.

APPENDIX C

SEMI-VOST METHOD INTERFERENCES/ARTIFACT FORMATION

INTRODUCTION

To investigate the possibility of formation of artifacts on XAD-2® resin or of the occurrence of artifacts from the decomposition of the XAD-2® resin or other processes, data developed during the laboratory generator studies (Appendix B) were examined for the occurrence of artifacts in the XAD-2® extracts. A computerized literature search was also performed in order to investigate any reports of the occurrence of artifacts in studies performed using XAD-2®.

EXAMINATION OF RADIAN-GENERATED DATA

Compounds which were spiked on XAD-2® resin for a study which involved variation in generator conditions included 1,4-dioxane, pyridine, toluene, urethane, chlorobenzene, 1,1,2,2-tetrachloroethane, phenol, nitrobenzene, hexachloroethane, naphthalene, resorcinol, and pentachlorophenol. Generator conditions which were varied included concentration of oxides of nitrogen, sample size, the concentration of sulfur dioxide, the concentration of HCl, moisture, hydrocarbon concentration, and sample flow rate. The original dataset was generated by GC/MS analysis in the full scan mode to determine compound recoveries under the various sets of generator conditions. However, to assess the possible formation of artifacts, eight sets of data generated by GC/MS analysis of XAD-2® extracts were examined for the presence of compounds other than spiked compounds, deuterated surrogate compounds, and the quantitation standard. The presence of any additional peaks might be attributed to the formation of artifacts.

Several solvent blanks were analyzed with the XAD-2® extracts and a chromatogram representative of the blanks is shown in Figure C-1. Compounds other than surrogate and quantitation standards which are

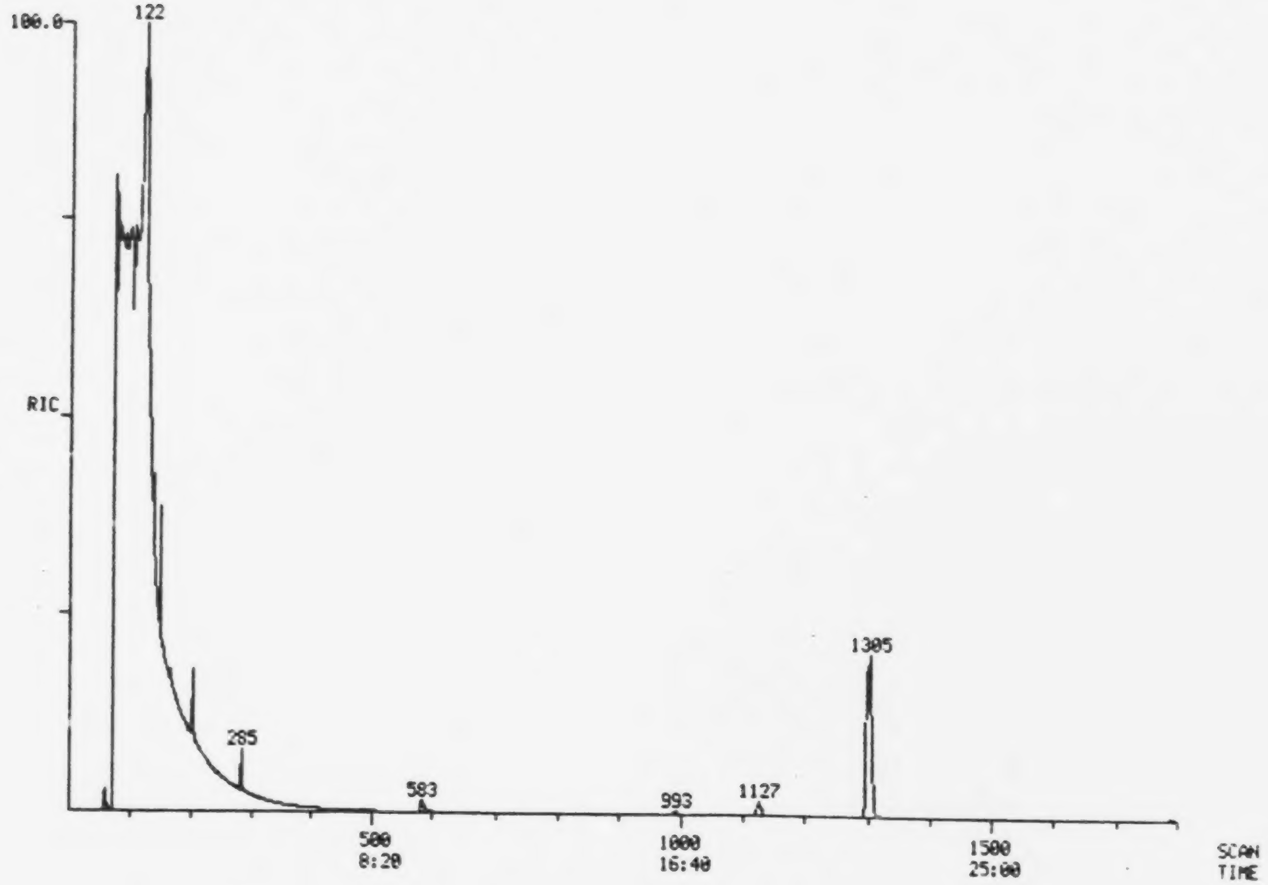


Figure C-1. Reconstructed gas chromatogram of a blank, with d_8-toluene (scan 203), carbon tetrachloride (scan 285), naphthalene (scan 583), dimethyl phthalate (scans 993 and 1127), and d_{10}-anthracene (scan 1305).

present in the blank can be attributed to a very low level of contamination. Figure C-2 shows a reconstructed gas chromatogram of a typical XAD-2® extract, and Table C-1 lists compounds which were typically identified in the XAD-2® extracts. These three analyses are typical of the 18 performed. The spiked compounds, deuterated surrogate compounds, and quantitation standard account for the majority of the peaks observed.

Of the remaining peaks, phthalate esters were identified which are plasticizers and are very often encountered as common solvent contaminants. Hexanol was observed in the blank and cannot thus be rationalized as coming exclusively from XAD-2® extracts. Volatile compounds such as chloroform, cyclohexane, and xylenes (always present at very low levels by comparison to the spiked compounds) are more readily explained as being contamination rather than by XAD-2® artifact formation due to their chemical structure. Fatty acid methyl esters are also frequently observed in the XAD-2® extracts at very low levels but it is difficult to rationalize an origin for these esters from decomposition of the resin or reaction of compounds with XAD-2® or spiked compounds. There is likewise no evidence such as the presence of substantial amounts of extraneous compounds to support the theory of possible formation of artifacts by interaction of the compounds with the extracting solvent.

The various generator conditions used to produce these samples do not seem to influence either type or quantity of artifact formation. The data clearly illustrate that formation of artifacts which can be extracted and analyzed by capillary gas chromatography/mass spectrometry does not appear to occur to any significant extent under the experimental conditions employed. Some of the compounds spiked, however, exhibit consistently poor recoveries. If these poor recoveries are due to formation of an artifact or occurrence of a chemical reaction, the resulting compound(s) may not be sufficiently volatile to be observed under the analytical conditions used.

SURVEY OF THE PUBLISHED LITERATURE

A computerized search of the available chemical literature yielded very little information pertinent to the question of artifact formation in the use/extraction of XAD-2®. Comparative evaluations of XAD-2® and

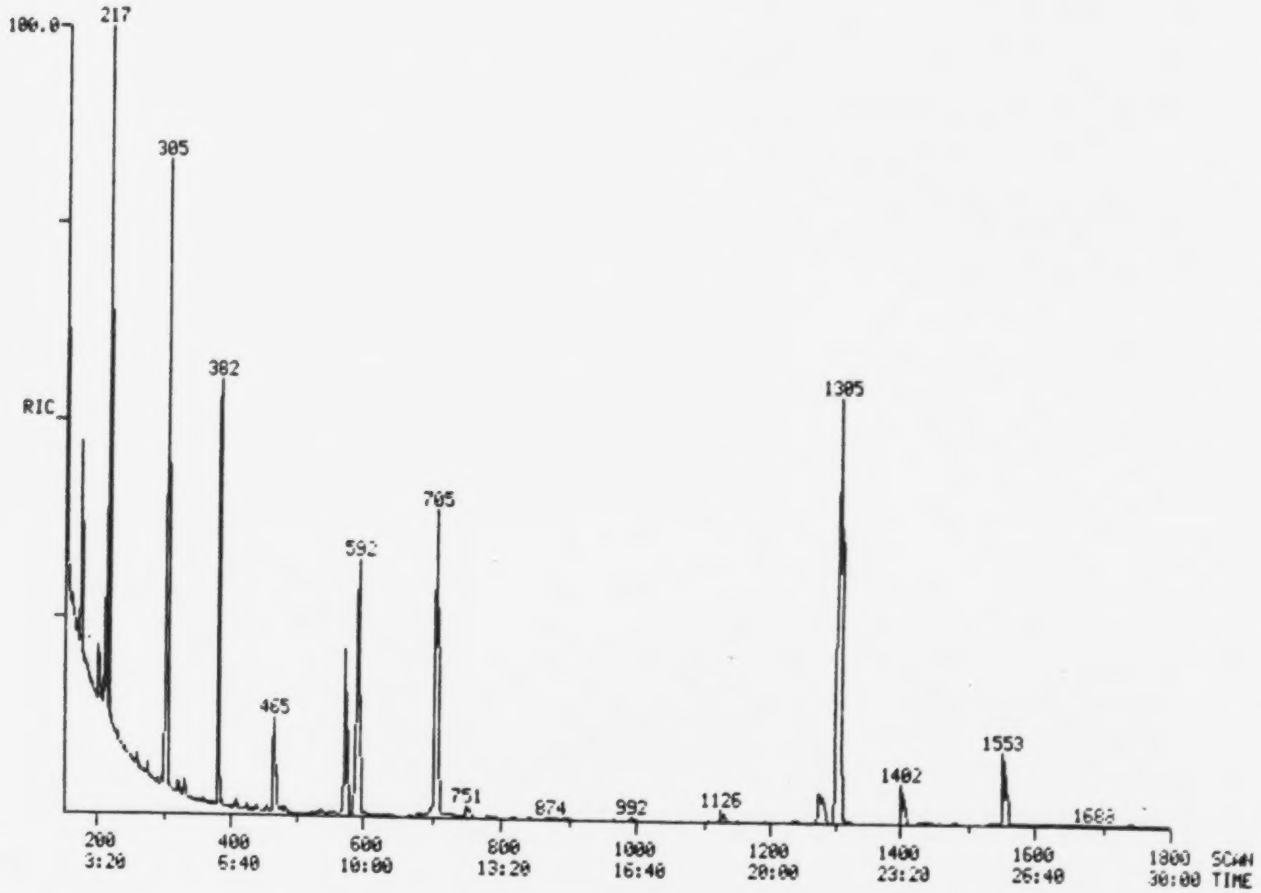


Figure C-2. Reconstructed gas chromatogram of a representative XAD-2® extract (normalized beyond the elution of the solvent peak). Peaks are identified in Table C-1. Very few extraneous peaks are observed, and the extraneous peaks which are identified arise more probably from contamination than from artifact formation.

TABLE C-1. COMPOUNDS IDENTIFIED IN ANALYSES OF XAD-2® EXTRACTS

cd-b XAD compound (scan)	abcd-b XAD compound (scan)	acde-b XAD compound (scan)
Chloroform (126)	Chloroform (140)	Cyclohexane (138)
1-Hexanol (138)	Hexanol (154)	1,4-Dioxane (155)*
2-Hexanol (180)	1,4-Dioxane (175)*	Hexanol (182)
d_8-Toluene (184)†	d_8-Toluene (213)†	Toluene (189)*
Toluene (187)*	Toluene (217)*	Chlorobenzene (262)*
Chlorobenzene (259)*	Chlorobenzene (305)*	Tetrachloroethane (223)*
Xylene (287)	Xylene (331)	Xylene (291)
Tetrachloroethane (346)*	Tetrachloroethane (382)*	Tetrachloroethane (350)*
Phenol (439)*	Phenol (465)*	Phenol*, d_5-Phenol† (444)
Hexachloroethane (556)*	Unknown (408)	Siloxane, column artifact (463)
Nitrobenzene (577)*	Hexachloroethane (571)*	Hexachloroethane (559)*
Naphthalene (695)*	Nitrobenzene (592)*	Nitrobenzene (580)*
Dimethyl phthalate (990)	Naphthalene (705)*	Naphthalene (699)*
Diethyl phthalate (1125)	Benzothiazole (751)	Benzothiazole (748)
Pentachlorophenol (1276)*	Diethyl phthalate (1126)	Dimethyl phthalate (993)
Methyl pentadecanoic acid, methyl ester (1401)	Pentachlorophenol (1276)*	Diethyl phthalate (1128)
Heneicosanoic acid, methyl ester (1552)	Methylpentadecanoic acid, methyl ester (1402)	Pentachlorophenol (1281)*
Unknown (1738)	Methylheptadecanoic acid, methyl ester (1553)	d_{10}-Anthracene (1307)§
d_{10}-Anthracene (1304)§	3-Methyl-2,6-dioxo-4 hexenoic acid (1740)	Methylpentadecanoic acid, methyl ester (1404)
	d_{10}-Anthracene (1305)§	Methylheptadecanoic acid, methyl ester (1556)

* Compounds spiked on XAD-2®.

† Deuterated surrogate compounds.

§ Quantitation standard.

other adsorptive media are abundant, but only specific recoveries for compounds of interest are reported in the literature. For most experiments, if recovery from XAD-2® for a compound of interest is not good, another medium which exhibits better recoveries is used instead of XAD-2 and reasons for poor recovery are not explored. However, observation of artifacts from XAD-2 are reported under certain conditions of extraction.

R.L. Hanson et al. (Evaluation of Tenax-GC® and XAD-2® as Polymer Adsorbents for Sampling Fossil Fuel Combustion Products Containing Nitrogen Oxides. R.L. Hanson, C.R. Clark, R.L. Carpenter, and C.H. Hobbs. Environ. Sci. Technol., 15, 701-705 (1981)) observe that both of the polymers examined decompose in the presence of oxides of nitrogen which are present in combustion effluent streams. Compounds reported from NO exposure include benzoic acid, ethylbenzaldehyde, dimethylbenzaldehyde, ethylphenylethanone or C_5-alkylbenzene, dimethylbenzoic acid, C_3-alkylbenzoic acid, hydroxnitrobenzoic acid, diethyl phthalate, diphenoxybenzene, and dibutyl phthalate. Compounds reported for NO_2 exposure included benzoic acid, ethylbenzaldehyde, C_4-alkybenzene, nitrophenol, ethylbenzoic acid, ethyl benzoate or ethoxyethylbenzene, and dinitrotoluene. None of these compounds were observed in the data from the Radian generator study, but most of the oxygen-containing compounds were observed in the qualitative analysis of the mass spectral data obtained from the Sauget field study (See Appendix F). None of the nitrated compounds, however, were observed in the field study, and no exhaustive examination of the Sauget data has been performed to determine if the oxygenated compounds are restricted to XAD-2® extracts.

R. Care et al. (On the Limits of Detection of Traces of Volatile Organics in Water, Using Amberlite XAD-2® Resin. R. Care, J.D. Morrison, and J.F. Smith. Water Res., 16, 663-665 (1982)) find that cleaned XAD-2® resin continues to release a large number of volatile organic compounds, mainly aromatic hydrocarbons, at low concentrations when extracted with ether after water is passed through the resin. The water appears to release these compounds. Although water was not used directly in the XAD-2® preparation or extraction process in either the generator study or the Sauget field study, relatively large amounts of water were trapped by the XAD-2® resin. Again, no significant amounts of aromatic hydrocarbons were observed in the data obtained in the generator study, but the qualitative analysis of the Sauget field data shows extensive numbers of alkylated aromatic hydrocarbons which could be released from the XAD-2®, present in the combustion products from the stack, or both.

H.A. James et al. (Impurities Arising from the Use of XAD-2® resin for the Extraction of Organic Pollutants in Drinking Water, H.A. James, C.P. Steel, and I. Wilson. J. Chromatogr., 208, 89-95 (1981)) observe a series of n-alkanes (C_{10} - C_{24}) as a series of impurities. When no water was used in the overall procedure, these compounds could be eliminated. The authors conclude that the impurities come from the resin but are released from the resin only when the resin is in contact with water. Again, no significant amounts of n-alkanes are observed in the examination of the generator data, but these compounds are observed in the qualitative analysis of the Sauget field data, possibly due to the amounts of water entrapped in the XAD-2® resin or possibly as combustion products.

In one report (Collection and Recovery of Organics from Water Using XAD-2® and XE-347 Resins. EPA-600/9-81-018) a small systematic study of recovery of a few types of organic compounds by solvent extraction from XAD-2® resin was reported, and the general trends are consistent with our observations from the generator study. The summary is shown below.

Compound	Recovery by extraction from XAD-2® resin (percent)
1,2,3-Trichloropropane	73
Naphthalene	75
Diethyl phthalate	78
Acridine	91
Phenol	38
Dodecane	15
Pyrrole	1

These results are consistent with our observations that the more polar, water-soluble compounds recover more poorly than non-polar compounds which are not water-soluble. For example, pyridine and pyrrole, chemically similar compounds, both exhibit very poor recoveries for reasons as yet unknown.

Formation of NO_x Artifacts in Aqueous Sample Fractions

An analysis of variance for the laboratory flue gas generator data set indicated that increases in flue gas NO_x levels were associated with decreases in the recoveries of 1,4-dioxane, urethane, and phenol in the aqueous compound fractions of the Semi-VOST train.

If nitration is a route of loss of spiked compounds, nitrophenols would be the products of the reaction for phenol and these compounds should be found in the back components of the sampling train. Accordingly, several extracts of back train components from the generator study were examined for the presence of nitrophenols. No traces of mono- and dinitrated phenols were found. However, the chromatographic elution of nitrophenols are poor. Further analyses of the generator data sets are warranted to evaluate NO_x-compound interactions with urethane and 1,4-dioxane.

CONCLUSIONS

On the basis of the data from the Radian generator study, the conclusion can be drawn that artifact formation is not a significant process. Analysis of XAD-2® extracts shows no significant peaks which can be interpreted as arising from the formation of artifacts. None of the compounds reported as possible XAD-2® artifacts in the literature were observed in the data from the generator study. However, most of the XAD-2® artifacts reported in the literature were formed because of significant amounts of water in the preparation/extraction process, and no water was used in the extraction of the XAD-2® for the generator study.

APPENDIX D
ANALYTICAL PRECISION AND BIAS

INTRODUCTION

In determining the overall precision of the Semi-VOST procedure, it is instructive to examine the precision of each step which may significantly affect the overall precision. The Semi-VOST procedure may be generalized as shown in Figure D-1 consisting of a sampling step, generally done at a site in the field; a sample preparation step; and an analysis step. The latter two steps are done in the laboratory.

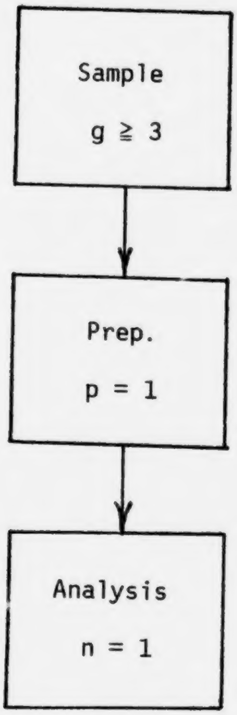
In Figure D-1, g is the number of samples taken and is usually three or greater. The samples may be taken simultaneously or consecutively. Each method introduces a different and characteristic set of variabilities. The number of sample preparations per sample, p, is usually 1, and in the case of the Semi-VOST procedure involves extraction of the XAD-2® resin and Kuderna-Danish (K-D) concentration. The number of analyses per sample preparation for the Semi-VOST process is n. The Semi-VOST analysis is specified to be done on a gas chromatograph/mass spectrometer (GC/MS). Other symbols in Figure D-1 are defined below:

X_i = an analytical determination, i;

$\bar{X}$ = the mean analytical result = $\sum_{i=1}^{N} X_i/N$;

N = npg, the total number of analytical determinations;

s_x^2 = the estimated variance of the analytical determinations = $\sum_{i=1}^{N} (X_i-\bar{X})^2/(N-1)$;


Sample
g ≧ 3
Prep.
p = 1
Analysis
n = 1

$$\text{Var. }(\bar{X}) = \frac{s_x^2}{npg} = \frac{s_G^2}{g} + \frac{s_p^2}{pg} + \frac{s_A^2}{npg}$$

$$\text{Var }(X_i) = s_x^2 = nps_G^2 + ns_p^2 + s_A^2$$

$$\bar{X} = \sum_{i=1}^{N} \frac{N_i}{N};\ N = npg;\ s_x^2 = \sum_{i=1}^{N} \frac{(X_i - \bar{X})^2}{N-1}$$

Figure D-1. Generalized Semi-VOST procedure.

$\mathrm{Var}(\bar{X})$ = the variance of the mean value of X_i;

$\mathrm{Var}(X_i)$ = the variance of X_i;

s_p^2 = the estimated variance of the preparation step(s);

s_A^2 = the estimated variance of the analytical determinations; and

s_G^2 = the estimated variance of the sampling step.

Four sets of studies were conducted to determine the components of variance described above. These studies are diagrammed schematically in Figure D-2. The Minimum Detection Limit (MDL) study provided the GC/MS estimates for the analytical variance, s_A^2. These studies were done first and were replicated six to eight times at each of four concentrations. The second set of studies was designed to determine the sample preparation variance, and is shown in Figure D-2 as the "Semi-VOST Analytical Precision Laboratory Evaluation." The third study is labeled the "Generator Study" and was conducted in the laboratory to determine the effects of several variables (moisture, sample volume, organic concentration, NO_x concentration, and sample flow rate). The generator study also provided a sampling variance estimate s_G^2 when combined with the MDL analytical variance and sample preparation variances, as described below.

The final set of measurements was taken in the field study and provided a measure of overall method precision as well as a typical field sampling variance estimate. The results and methods of calculation are described below.

In determining an overall precision for the Semi-VOST procedure, the results for chlorobenzene were examined in detail in all the studies described above because chlorobenzene was detected in all the field study samples taken for determining method precision.

SUMMARY PRECISION RESULTS

Summary precision results are given in Table D-1 for chlorobenzene. The overall variability is separated into three components - sampling, sample preparation, and GC/MS analysis - in terms of percent of total variance and percent CV for each component. For the Analytical Laboratory

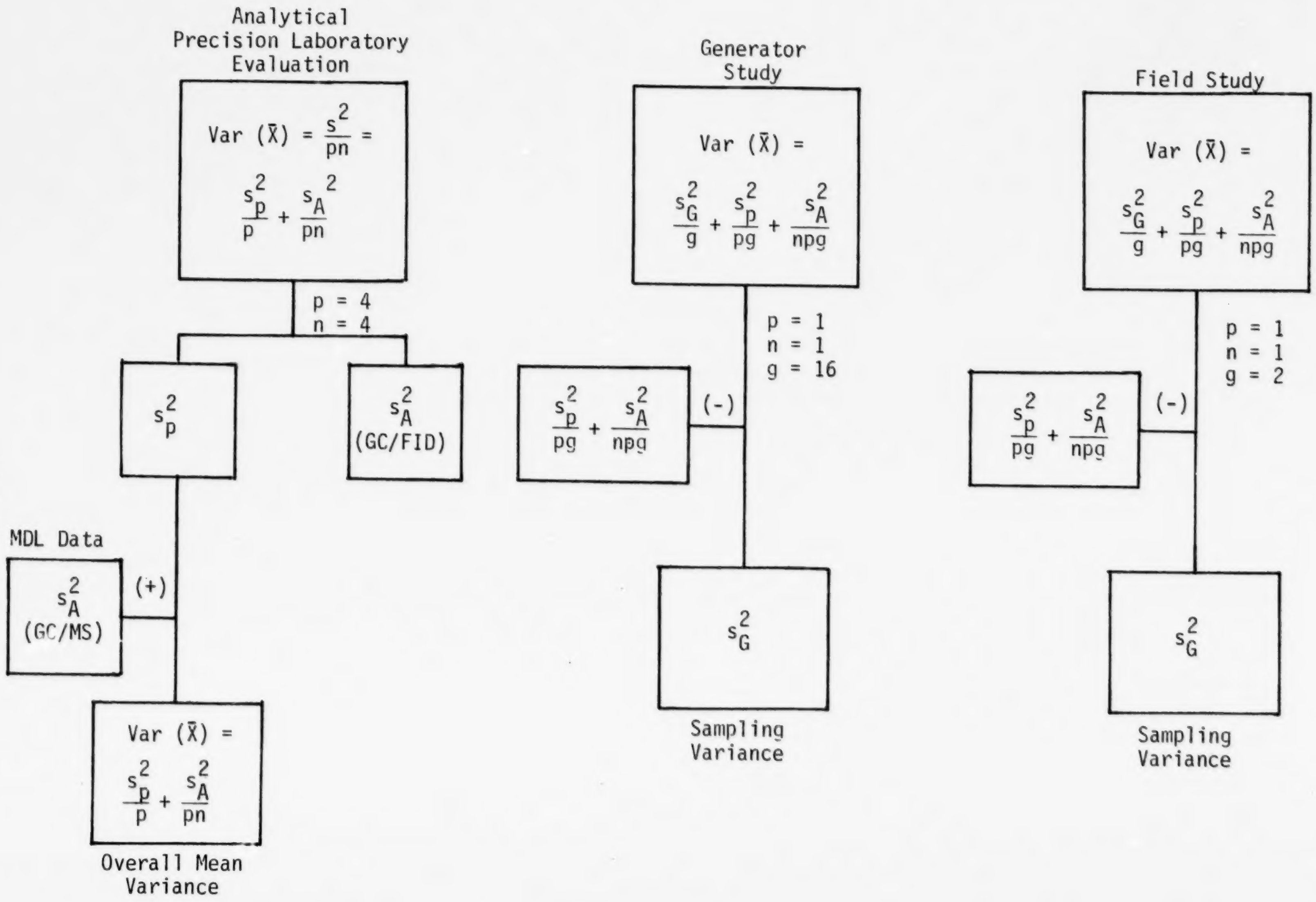

Analytical Precision Laboratory Evaluation
$\mathrm{Var}(\bar{X}) = \frac{s^2}{pn} = \frac{s_p^2}{p} + \frac{s_A^2}{pn}$
$p = 4$
$n = 4$
s_p^2
s_A^2 (GC/FID)
MDL Data
s_A^2 (GC/MS)
(+)
$\mathrm{Var}(\bar{X}) = \frac{s_p^2}{p} + \frac{s_A^2}{pn}$
Overall Mean Variance
Generator Study
$\mathrm{Var}(\bar{X}) = \frac{s_G^2}{g} + \frac{s_p^2}{pg} + \frac{s_A^2}{npg}$
$p = 1$
$n = 1$
$g = 16$
$\frac{s_p^2}{pg} + \frac{s_A^2}{npg}$
(-)
s_G^2
Sampling Variance
Field Study
$\mathrm{Var}(\bar{X}) = \frac{s_G^2}{g} + \frac{s_p^2}{pg} + \frac{s_A^2}{npg}$
$p = 1$
$n = 1$
$g = 2$
$\frac{s_p^2}{pg} + \frac{s_A^2}{npg}$
(-)
s_G^2
Sampling Variance

Figure D-2. Separation and combination of components of variance.

TABLE D-1. APPORTIONMENT OF METHOD PRECISION FOR CHLOROBENZENE

	Analytical Laboratory Precision Evaluation with GC/MS			Generator study		Field study	
	% Total variance*	% Total variance†	% CV*,§	% Total variance	% CV	% Total variance	% CV
Sampling	-	-	-	11.4	3.8	78.5	17.1
Sample preparation	6.4	21.6	2.7	5.7	2.7	1.4	2.3
GC/MS analysis	93.6	78.4	10.2	82.9	10.3	20.1	8.6
Overall	100.0	100.0	11.6	100.0	11.3	100.0	19.9

Assumptions:

- GC/MS analytical variance from MDL study applicable in these studies.
- GC/MS instrument response linear function of composition.
- GC/MS sample variance linear function of composition.
- (Sample preparation variance/GC/MS analytical variance) = constant for p = 1, n =1.

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* Number of preparations, p = 1; number of analyses per preparation, n = 1.

† Number of preparations = 4; number of analyses per preparation = 4.

§ % CV is percent coefficient of variation = $(s_x/\bar{X}) \times 100$.

Precision Evaluation (four preparations with four analyses per preparation) using the GC/MS analytical variance estimate, the overall precision was 11.6 percent in terms of percent CV. Table D-1 indicates that if the Analytical Laboratory Precision Evaluation was determined with four preparations and with four analyses per preparation, the percentage of the total variance that would be due to the preparation is 21.6 percent, while the GC/MS analytical variance would be 78.4 percent of the total variance. For the preparations and analyses used in the generator study and in the field study, the number of preparations per sample and analyses per preparation are both one. The preparation variance is 6.4 percent of the total variance, while the GC/MS analytical variance would be 93.6 percent of the total variance. The ratio of these two variances (6.4/93.6) was assumed to be constant for chlorobenzene for the generator study and for the field study.

The overall precision estimates for the generator study and the field study were 11.3 and 19.9 (percent CV), respectively. Sampling variance increased from 11.4 to 78.5 percent of the total variance when comparing the generator studies with the field studies. Percent CV is not additive within a particular study, but percent of total variance is additive.

MDL DETERMINATION

The MDL was determined by GC/MS analysis for a mixture of 12 compounds in methanol. The results are given in Table D-2. The method of Glaser, et al. [Glaser, John A., Denis L. Foerst, Gerald D. McKee, Stephen A. Quave, and William L. Budde, "Trace Analysis for Wastewaters," Environmental Science and Technology, 15, (12), 1426 (1981)] was followed in determining MDL. The 12 compounds were mixed in a solution of methanol at an estimated MDL of about 25 ng/μL for each compound. Seven replicate analyses were performed on the GC/MS. Based on the means and standard deviations of the area counts for each compound, a newly estimated MDL was calculated using Glaser's method for each compound and a new solution was mixed at the newly estimated MDL. Four successive iterations were performed, each at a lower concentration for each compound. Glaser's MDL determination is based on the hypothesis that as the concentration decreases,

TABLE D-2. MINIMUM DETECTION LIMIT (MDL) FOR GC/MS ANALYSIS OF TEST COMPOUNDS IN METHANOL

	ng/μL
1,4-Dioxane	7.0
Pyridine	8.5
Toluene	1.9
Urethane	10.0
Chlorobenzene	0.37
1,1,2,2-Tetrachloroethane	0.25
Phenol	5.0
Hexachloroethane	0.90
Nitrobenzene	1.1
Naphthalene	0.32
Resorcinol	7.3
Pentachlorophenol	4.2

the variance of the response variable (i.e., area counts for the GC/MS) increases. For the GC/MS and all the 12 compounds used in this study, the standard deviation (square root of the variance) decreased as the concentration decreased, as can be seen in Table D-3 for chlorobenzene. As a result, Glaser's definition of MDL was modified, and is given in Equation D-5 below.

Part of Glaser's procedure involved injecting solvent blanks between each of the replicate analyses. A maximum blank peak was read in the scan range for each compound in each solvent blank. Thus, a mean, $\bar{X}_B$, and standard deviation, s_B, of seven replicate blank readings were determined for each compound. The maximum blank readings and the sample readings for each compound were assumed to be normally distributed. Figure D-3 shows the distributions of the blanks and samples plotted on a horizontal concentration scale. The variables are defined below Figure D-3 and MDL is defined in Equation D-5.

To calculate X_{CB}:

s_B = standard deviation of peak heights for blank readings,
s_S = standard deviation of peak heights for sample readings,
n_B = number of replicates for blank readings,
n_S = number of replicates for sample readings, and
$t_{(n-1),(1-\alpha)}$ = Student's t statistic with (n-1) degrees of freedom and α level of significance.

$$t_{(n_B-1),\ 0.99} = \frac{X_{CB} - \bar{X}_B}{s_B/\sqrt{n_B}} \qquad \text{(D-1)}$$

$$X_{CB} = \bar{X}_B + t_{(n_B-1),\ 0.99}\ s_B/\sqrt{n_B} \qquad \text{(D-2)}$$

Similarly, to calculate X_{CS}:

$$X_{CS} = \bar{X}_S + t_{(n_S-1),\ 0.99}\ s_S/\sqrt{n_S} \qquad \text{(D-3)}$$

At MDL, $X_{CS} = X_{CB} = X_C$, or $(X_{CS} - X_{CB}) = 0$

$$\bar{X}_B + t_{(n_B-1),\ 0.99}\ s_B/\sqrt{n_B} = \bar{X}_S - t_{(n_S-1),\ 0.99}\ s_S/\sqrt{n_S} \qquad \text{(D-4)}$$

TABLE D-3. GC/MS CHLOROBENZENE RESULTS

Run no.	X ng/μL	$\bar{Y}$ mean area count	Std dev, area count, s	% CV	n	$\hat{Y}$*	$\hat{s}$†	% CV§
1	26.85	19,074.0	2,314.1	12.1	7	19,106.2	1,705.0	8.92
2	8.70	6,148.0	557.5	9.07	8	6,148.3	559.9	9.11
3	1.34	895.9	114.0	12.7	7	893.7	95.58	10.69
4	0.225	95.83	9.24	9.64	6	97.7	25.23	25.82

Using only Runs 2, 3, and 4:

$$\hat{Y} = -62.92930897 + 713.9325793X$$

Correlation coefficient, R = 0.999999809

$$\hat{s} = 11.0404616 + 63.08997713X$$

Correlation coefficient, R = 0.998224731

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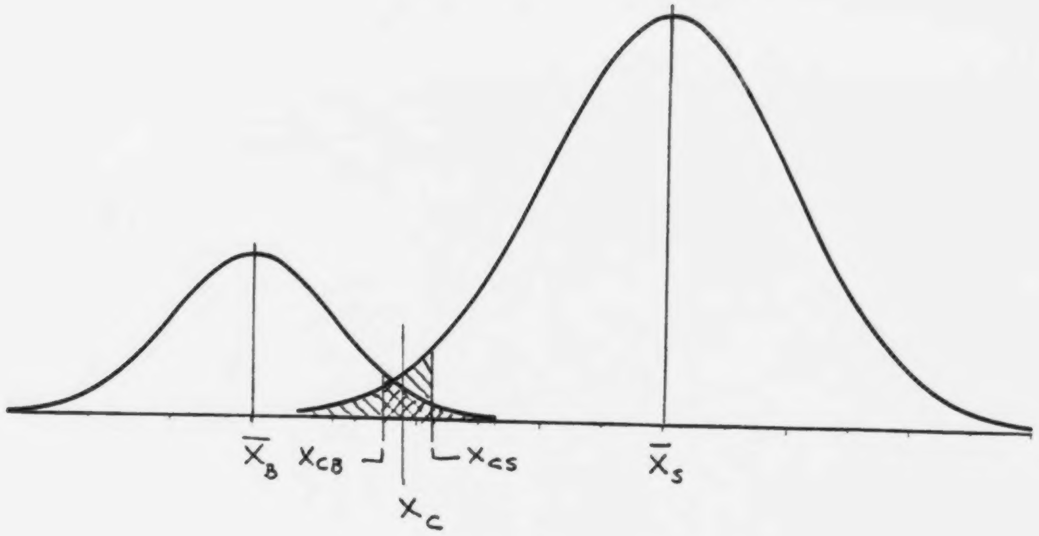
* $\hat{Y}$ denotes value of Y calculated from regression equation given.

† $\hat{s}$ denotes value of s calculated from regression equation given.

§ % CV = $(\hat{s}/\hat{Y}) \cdot 100$.



Given:

$\bar{X}_B$ = mean value of the peak height (or area count) for blank readings,

$\bar{X}_S$ = mean value of the peak height (or area count) for sample readings,

X_{CB} = critical value of the peak height such that $P\ (X_S \leq X_{CB}) = 0.99$,

X_{CS} = critical value of the peak height such that $P\ (X_S \geq X_{CS}) = 0.99$,

X_C = critical value of peak heights (at MDL) when $X_C = X_{CS} = X_{CB}$,

Figure D-3. MDL determination.

Define

$$\mathrm{MDL} \equiv \bar{X}_S = \bar{X}_B + t_{(n\ -1),\ 0.99}\ s_B/\sqrt{n_B} + t_{(n\ -1),\ 0.99}\ s_S/\sqrt{n_S}$$

(D-5)

B S

The procedure for calculating MDL is outlined below.

1. For each iteration, and for each compound, beginning with the mixture having 25 ng/µL for each component, calculate $\bar{X}_B$, $\bar{X}_s$, s_B, and s_S, the means and standard deviations for the blank readings and sample readings, respectively.
2. Calculate X_{CB} and X_{CS} from Equations D-1 and D-2, respectively. Student's t statistic is tabulated in most statistics texts.
3. For each iteration, calculate $(X_{CB} - X_{CS})$ which can either be positive or negative ($(X_{CB} - X_{CS})$ is shown to be positive in Figure D-3).
4. Plot $(X_{CB} - X_{CS})$ vs. $\bar{X}_S$ and extrapolate (or interpolate) to the $\bar{X}_S$ at which $(X_{CB} - X_{CS}) = 0.0$.
5. MDL is defined as the value of $\bar{X}_S$ when $(X_{CB} - X_{CS}) = 0$.

The variable X_{CS} is calculated by Equation D-2 and is the value of X_S, the peak height (or area count) for a sample reading, such that the probability is $(1-\alpha)$ that all other readings of X_S are greater than X_{CS}. In the definition of MDL in this study, α was chosen to be 0.01. The variable X_{CB} is the value of X_B such that the probability is $(1-\alpha)$ that all other readings of X_B are less than X_{CB}.

For chlorobenzene, more detailed results are given in Table D-3. Columns 2 and 3 of the table are the experimentally determined values of concentration (ng/µL) and mean area counts, respectively. Column 4 gives the standard deviation of the area counts for each run. Column 5 gives the replications per run. Smoothed values of $\hat{Y}$ and $\hat{s}$ were calculated from the regression equations shown. The $\bar{Y}$ and s values for Run 1 were not used in the regression equations for estimation of percent

CV because the results were negative for $\hat{s}$, at $x = 0.225$ ng/µL, which is not realistic. The significant results of this study are that both s_A and percent CV are functions of concentration for chlorobenzene.

LABORATORY ANALYTICAL PRECISION, BIAS, AND SAMPLE PREPARATION EVALUATION

Four test series were performed in this study and are summarized in Table D-4. Standard solutions containing about 260 µg of each of three target compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) were spiked into four sets of apparatus as shown in Table D-4. The samples were prepared for analysis either by K-D concentration only for Series 1, or first by extraction followed by K-D concentration for Series 2 and 3. Each apparatus was analyzed by four injections into a GC/FID instrument. Additional details of the tasks are given below.

Series 1 runs involved injecting about 250 µg (260 µg toluene, 266 µg chlorobenzene, and 254 µg 1,1,2,2-tetrachloroethane) of each target compound into about 250 mL of methylene chloride and reducing the volume in a K-D apparatus to less than 5 mL. One hundred microliters of an o-xylene (19.7 µg o-xylene) solution were added as an internal standard to the K-D apparatus concentrate and the solution made up to 5.0 mL with methylene chloride solvent. The solution was then analyzed in quadruplicate using an autosampler to inject the solution into the GC/FID apparatus. Four sets of K-D apparatus were run in Series 1, in parallel.

In Series 2, four sets of XAD-2® resin beds were injected with a nominal 250 µg of each target compound. Each bed was extracted with methylene chloride in a Soxhlet extraction apparatus, and reduced in volume to 5.0 mL using a K-D apparatus. Each K-D concentrate was spiked with 100 µL of the o-xylene internal standard and analyzed in quadruplicate using the autosampler to inject the solution into the GC/FID apparatus.

Series 3 simulated the single set of water impinger extractions in a Semi-VOST apparatus. About 250 µg of each target compound were injected into about 250 mL of water. The water was adjusted to a pH of about 1.0 and extracted with methylene chloride, followed by basic extraction (water pH of 11). The acid and base extracts were combined and reduced

TABLE D-4. LABORATORY PRECISION AND RECOVERY STUDIES

Series	Number of replicates	Standard solution spiked into	Extraction	K-D concentration	GC/FID injection method	Analytical replicates per K-D concentrate
1	4	K-D solution	None	Yes	Autosampler	4
2	4	XAD-2®	Soxhlet	Yes	Autosampler	4
3	4	Water	Separatory funnel	Yes	Autosampler	4
1	4	K-D solution	None	Yes	Manual	4

to 5.0 mL in a K-D apparatus. One hundred μL of o-xylene internal standard were added to each concentrated extract and each was analyzed in quadruplicate, using the autosampler to inject the solution into the GC/FID apparatus.

Series 1 described above was repeated using manual injections into the GC-FID rather than using the autosampler.

Precision and Recovery Results, Laboratory Precision Determination

The precision and recovery results are summarized in Table D-5 for the four sets of procedures described above. The means given in Columns 2 and 3 record the averages of 16 determinations of each compound's recovery for each task (four repeated analyses from each of four sets of apparatus). Column 2 gives the area counts and Column 3 reports the concentrations in μg/mL. Column 4 gives percentage recovery. The amount of each target compound contained in each apparatus in each task is given in the footnote "*" of Table D-1. The percent recovery is calculated by dividing the μg/mL recovered (the mean value in Column 3) by the amount injected (spiked) into each apparatus and multiplying the quotient by 100. This is the only measure of accuracy that was possible in this set of experiments.

Series 1 and 2 all report percent recoveries near 100 percent for all three target compounds. Series 3 involving water extractions, however, shows percent recoveries ranging from 56 to 84 percent.

The analytical variance estimate (and its square root, the standard deviation) was separated from the treatment variance by a standard one-way analysis of variance. The "Treatment" for Series 1 was simply the variance of the K-D concentration step. For Series 2, the "Treatment" standard deviation included the XAD-2® extraction and subsequent K-D concentration to 5 mL. For Series 3, the treatment standard deviation included the separatory funnel extractions, followed by the K-D concentration steps.

Columns 5 and 6 give results of the standard deviation determinations for the GC/FID analyses. Column 5 gives the standard deviations in area counts for the four repeated analyses and the four apparatuses used in each task. Column 6 shows μg/mL determined from the area counts.

TABLE D-5. LABORATORY ANALYTICAL PRECISION AND SAMPLE PREPARATION AND RECOVERY RESULTS

				GC/FID analysis			Sample preparation		
	Mean			Std. deviation			Std. deviation		
	Area counts	μg/mL	Percent recovery*	Area counts	μg/mL	Percent CV	Area counts	μg/mL	Percent CV
Series 1, Autosampler Injections (AsI), K-D Concentration + Analysis									
Toluene	42,183	53.2	102.0	307	0.387	0.73	1,717	2.16	4.07
Chlorobenzene	31,134	56.4	106.0	220	0.399	0.71	1,027	1.86	3.30
1,1,2,2-Tetrachloroethane	6,881	55.7	110.0	54	0.437	0.78	245	1.98	3.56
Series 2, AsI, XAD-2® Extraction, K-D Concentration + Analysis									
Toluene	40,114	47.9	92.1	547	0.653	1.36	706	0.84	1.76
Chlorobenzene	31,223	53.6	101.0	244	0.419	0.77	597	1.02	1.88
1,1,2,2-Tetrachloroethane	6,825	53.3	105.0	55	0.429	0.80	141	1.10	2.06
Series 3, AsI, Separatory Funnel Extraction, K-D Concentration + Analysis									
Toluene	27,612	29.2	56.1	196	0.207	0.71	2,457	2.60	8.90
Chlorobenzene	22,680	34.2	64.2	206	0.310	0.91	1,954	2.94	8.61
1,1,2,2-Tetrachloroethane	6,521	42.8	84.3	43	0.285	0.66	505	3.31	7.74
Series 1, Manual Injections, K-D Concentration + Analysis									
Toluene	51,609	46.5	89.5	1,085	0.979	2.10	2,082	1.88	4.03
Chlorobenzene	40,084	52.0	97.7	592	0.768	1.48	1,292	1.65	3.22
1,1,2,2-Tetrachloroethane	8,981	52.5	103.0	102	0.597	1.14	242	1.41	2.69

* Standard solution injected (spiked) into each apparatus contains the following:
Toluene - 260 μg in 5 mL; 52.0 μg/mL
Chlorobenzene - 266 μg in 5 mL; 53.2 μg/mL
1,1,2,2-Tetrachloroethane - 254 μg in 5 mL; 50.8 μg/mL

Column 7 shows the percent coefficients of variation obtained by dividing the analytical standard deviation by the mean recovery, e.g., Column 5/Column 2. This percent CV may be viewed as a precision measurement for the analysis step. The analytical percent CV figures for Series 1, 2, and 3 all appear to average around 0.8 with little variability within or between tasks (with the possible exceptions of toluene in Series 2 and chlorobenzene in Series 3).

The percent CV figures for the analytical standard deviations given in Table D-5 for Series 1, Manual Injections, indicate the analytical standard deviations to be a least twice the analytical standard deviation for Series 1, Autosampler Injections. The increase in percent CVs reflects the increased imprecision caused by manual injections compared to the autosampler injections. The sample preparation standard deviation percent CVs (the last column) for Series 1, Manual Injections, however, compare favorably with those of Series 1, Autosampler Injection runs.

The sample preparation results are given in three forms. Column 8 lists the sample preparation standard deviation area counts which are converted to µg/mL in Column 9. Percent coefficient of variation for the sample preparations in Column 10 gives the quotient of Column 8, the sample preparation standard deviation, divided by the mean area counts, Column 2. The last column in the table is a measure of the precision or variability of the procedure done in the task for a given compound after the analytical variability has been removed. For example, in Series 1 for toluene, the precision of the K-D concentration step is 4.07. The precisions of the K-D concentration step for chlorobenzene and 1,1,2,2-tetrachloroethane are 3.30 and 3.56 percent CV, respectively. As noted above, the precision in Series 1 for the K-D concentration step using manual injections into the GC/FID apparatus is not significantly different from the K-D concentration step when using the autosampler for injections into the GC/FID apparatus. In both cases, handling of the K-D apparatus is identical and a different precision is not to be expected.

For Series 2, the sample preparation standard deviations characterize the variability of the XAD-2® extraction step and K-D concentration step combined. The standard deviations for the extraction-concentration steps for the target compounds in Task C are less than the corresponding standard deviations for the concentration step alone in Series 2. Testing the hypothesis that for each compound the treatment variances for Series 1 and 2 are equal results in the conclusion that they are equal at the 5 percent level of significance. From a practical viewpoint, the variance of the K-D concentration step alone is not significantly different from the combined XAD-2® extraction and K-D concentration steps. In the calculations below, the standard deviations for each compound for Series 1 and 2 (both done with the autosampler) were pooled for the sample preparation step component of variance.

Sample preparation standard deviations for Series 3 give variabilities and precision measurements for the separatory funnel-K-D concentration steps, after having had the analytical variability removed from the results. These percent CV numbers range from three to five times larger than the Soxhlet extraction-K-D concentration variabilities. This result is not unexpected for at least two reasons: (1) the transfer of an organic compound from the water phase to an organic phase is slow and highly dependent on solubility, contact time, and degree of mixing of the phases, and (2) manual separation of the phases in a separatory funnel is difficult to achieve reproducibly. Obtaining comparable degrees of mixing of two phases in separatory funnels is also difficult to achieve reproducibly. Future experiments will be conducted to determine if multiple separatory funnel extractions improve sample preparation precision and reduce bias.

Because the mean values of the concentrations of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane for Series 1 are not significantly different from the means for Series 2, and because the treatment standard deviations for the same task are not significantly different, the means and standard deviations were pooled as shown below for chlorobenzene.

For the chlorobenzene mean,

$$\bar{X} = (31{,}134.3 + 31{,}223.4)/2 = 31{,}178.85 \text{ area counts}$$

For the chlorobenzene treatment (or preparation) standard deviation,

$$s_p = \surd\ (((1{,}026.9)^2 + (597.1)^2)/2) = 840 \text{ area counts}$$

The area counts for the analytical standard deviation for chlorobenzene in Table D-3 were not pooled because the analytical standard deviation in the table is for the GC/FID.

In order to determine the percent of the total variability due to sample preparation, a ratio of the sample preparation variance to the total method variance would be required. It was desirable also to determine the percent of the variability due to sampling, sample preparation, and analysis in the generator and field studies for chlorobenzene. Since the latter two studies used GC/MS for analysis, it would be necessary to estimate the GC/MS analytical variance that would have occurred in the laboratory analytical and sample preparation study so that all three studies would be comparable. Figure D-2 diagrams the steps involved. For the laboratory analytical and sample preparation precision and percent recovery evaluation, the overall variance was split into the sample preparation variance, s_p^2, and the GC/FID analytical variance. The GC/MS analytical variance from the MDL studies was then combined with the sample preparation variance to get an overall variance for the study if the GC/MS had been used for the analyses. The calculations involved are given below.

Because the concentration level for chlorobenzene for the laboratory precision and recovery determination runs was outside the range of concentrations in the MDL study, it was necessary to extrapolate the MDL data to determine s_A for chlorobenzene at $\bar{X} = 53.2$ ng/μL.

The following procedure was used to extrapolate s_A data for GC/MS:

1. calculate $\hat{Y}$ from regression equation, see Table D-3;
2. calculate $\hat{s}_A$ using only the data from Runs 1, 2, and 3;
3. calculate $\hat{s}_A$ using only the data from Runs 2, 3, and 4;
4. correct both values of $\hat{s}_A$ to 31,178.85 area counts for the generator study;
5. pool $\hat{s}_A$ values calculated in Step 4 by taking the geometric mean, round off;
6. calculate percent of total variance attributable to preparation and to analysis for n = 1, p = 1;

7. calculate percent of total variance attributable to preparation and to analysis for $n = 4$, $p = 4$; and

8. calculate precision for laboratory precision study for $n = 4$, $p = 4$.

The calculations follow and are numbered as indicated in the outline above.

Using Runs 1, 2, 3, and 4, the linear regression equation for chlorobenzene, see Table D-3.

1. @ 53.2 µg/mL, $\hat{Y} = 37{,}855.58388$

   actual $\bar{Y} = 31{,}178.85$

2. Using only Runs 1, 2, and 3 assuming $s_A = f(x)$

   @ 53.2 µg/mL, $\hat{s}_A = 4{,}554.916811$

3. Using only Runs 2, 3, and 4

   @ 53.2 µg/mL, $\hat{s}_A = 2{,}630.185937$

4. Correcting both to 31,178.85 area counts gives

   $$\frac{4{,}554.916811}{37{,}855.58388} \times 31{,}178.85 = 3{,}596.4225$$

   $$\frac{3{,}367.427245}{37{,}855.58388} \times 31{,}178.85 = 2{,}630.185937$$

5. Pooling estimates (i.e., taking geometric mean) = 3,150.566049

   Round off to $\hat{s}_A = 3{,}200$ @ $\bar{X} = 31{,}178.85$, % CV = 10.26

   $s_p = 840$, see above

6. For the case of one preparation and one analysis

   $$\begin{aligned} \mathrm{Var}\,(X_i) &= s_p^2 + s_A^2 \\ &= (840)^2 + (3{,}200)^2 \\ &= 10{,}945{,}600 \end{aligned}$$

   $s_x = 3{,}308.4$ overall variance (one preparation and one analysis)

Calculate proportion of total variance that is preparation for $n = 1$, $p = 1$

$$\frac{(840)^2\ (100)}{10{,}945{,}600} = 6.4 \text{ percent due to preparation}$$

Analysis = 93.6 percent due to analysis

7. For the laboratory study $p = 4$, $n = 4$

$$\text{Var } X = s_x^2 = ns_p^2 + s_A^2$$

$$s_x^2 = 4\ (840)^2 + (3{,}200)^2$$

$$s_x^2 = 13{,}062{,}400$$

$$s_x = 3{,}614.2$$

$$\frac{4\ (840)^2}{(3{,}614.2)^2} \times 100 = 21.6 \text{ percent preparation}$$

$$\frac{(3{,}200)^2}{(3{,}614.2)^2} \times 100 = 78.4 \text{ percent analysis}$$

8. Overall percent CV = $\frac{s_x}{\bar{X}} = \frac{3{,}614.2}{31{,}178.85} \times 100 = 11.6$ percent

These results are summarized in Table D-1.

Additional measurements were taken in the laboratory precision and sample preparation studies to determine if a nitrogen blowdown of the SML K-D concentrate from 5 mL to 2.5 mL would adversely change the solute concentrations of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane. Table D-6 shows the results of the studies. The results in row 1 of the table give the mean GC/FID area counts for the solutes at 5 mL total volume. Dry nitrogen was passed over the solution until the total volume was reduced to 2.5 mL. Eight additional GC/FID analyses were performed and the mean area counts for the solute are given in row 2 of Table D-6. The fact that the ratio of area count (row 2/row 1) was very close to 2.00 (see row 3) confirmed the fact that an insignificant amount of these solutes was lost by the reduction in volume.

TABLE D-6. N_2 VOLUME REDUCTION OF K-D CONCENTRATE

	Toluene	Chlorobenzene	1,1,2,2-Tetrachloroethane
5 mL $\bar{X}$*	30,657	21,431	4,637
2.5 mL $\bar{X}$	60,608	43,127	9,415
Ratio	1.98	2.01	2.03

* $\bar{X}$ = average of eight determinations, area counts.

GENERATOR STUDY PRECISION RESULTS

The generator study precision results are given in Table D-7. For chlorobenzene, the percent CV is 11.30. In the generator study, there were 16 samples, one preparation per sample, and one GC/MS analysis per preparation. For this procedure,

$$\mathrm{Var}\ (\bar{X}) = \frac{s_x^2}{gpn} = \frac{s_G^2}{g} + \frac{s_p^2}{pg} + \frac{s_A^2}{npg} \qquad \text{(D-3)}$$

or

$$\mathrm{Var}\ (X) = s_x = np\ s_G^2 + n\ s_p^2 + s_A^2 \qquad \text{(D-4)}$$

For $n = p = 1$

$$s_x = s_G^2 + s_p^2 + s_A^2 \qquad \text{(D-5)}$$

For the generator study, the mean concentration was

$$X = (1.11 + 3.70)/2 = 2.41\ \mathrm{ng/\mu L}$$

Using the regression equation in Table D-3,

$$@\ X = 2.41\ \mathrm{ng/\mu L} \qquad \hat{Y} = 1{,}658.15\ \text{area counts}$$

For generator study precision of 11.30 percent CV, overall

$$s_x = 0.1130\ (1{,}658.15) = 187.37\ \text{area counts}$$

@ $X = 2.41$ ng/μL, analytical percent CV = 10.29 (see Table D-3)

$$s_A = 0.1029\ (1{,}658.15) = 170.62\ \text{area counts.}$$

Assuming preparation variance/analytical variance = (6.4/93.6)

$$\frac{s_A^2}{s_p^2} = \frac{93.6}{6.4}$$

$$s_p = \sqrt{\frac{(170.62)^2\ 6.4}{93.6}} = 44.65$$

From equation D-5

$$(187.37)^2 = s_G^2 + s_p^2 + s_A^2 = s_G^2 + (44.65)^2 + (170.62)^2$$

$s_G = 63.27$, the sampling standard deviation

TABLE D-7. GENERATOR STUDY PRECISION*

Compound	Mean recovery, %	Std. dev., %	Precision, % CV
1,4-Dioxane	101	16.6	16.3
Pyridine	62	40.3	65.2
Toluene	94	26.9	29.7
Urethane	49	24.5	49.9
Chlorobenzene	99	11.2	11.3
1,1,2,2-Tetrachloroethane	105	13.3	12.6
Phenol	86	16.7	19.2
Nitrobenzene	111	9.0	8.1
Hexachloroethane	104	7.4	7.1
Naphthalene	107	11.4	10.7
Resorcinol	-	-	-
Pentachlorophenol	-	-	-

* Based on 16 preparations and one analysis for each preparation.

Calculate percent of total variance for each step of the procedure

1. sampling: $\frac{(63.27)^2}{(187.37)^2} \times 100 = 11.4$ percent

2. preparation: $\frac{(44.65)^2}{(187.37)^2} \times 100 = 5.7$ percent

3. GC/MS analysis: $\frac{(170.62)^2}{(187.37)^2} \times 100 = 82.9$ percent

Overall precision 11.30 percent, see Tables D-7 and D-1.

FIELD STUDY PRECISION RESULTS

Table D-8 summarizes the chlorobenzene precision results for the field study. Columns 2, 3, and 4 present the standard deviation, the mean, and the percent coefficient of variation (% CV) for the concentrations, corrected for blanks, of samples for the duplicated run pairs shown in Column 1. The final three columns in the table show the results, corrected for a deuterated spike that was put in the sample train after the completion of the sample and before the sample preparation step or analysis.

Below the chlorobenzene concentration values for runs 5B-5D are pooled values of the standard deviation, the mean, and the resulting percent CV. Pooled values in the row labeled (a) include all runs with the exception of the run pair 4B-4D. Pooled values in row (b) exclude run pairs 4B-4D, 1A-1B, and 2A-2B. The latter two pairs (runs 1A-1B and 2A-2B) were test runs in which a dynamic spike of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane was introduced into the Semi-VOST sample train by the Radian field crew. The purpose of the dynamic spike was to enable the calculation of a percent recovery of the spike as an accuracy measure.

Because the dynamic spike added to the overall variability of the chlorobenzene measurement, runs 1A-1B and 2A-2B were not included in the overall precision determination. Further, because neither the Generator Study nor the Laboratory Analytical Precision Determination used a deuterated spike, the data in the last three columns of Table D-7 were not used in characterizing the overall field study precision.

TABLE D-8. CHLOROBENZENE PRECISION RESULTS, FIELD STUDY

Run pair	Concentration, $\mu g/m^3$			Concentration, $\mu g/m^3$, corrected for deuterated spike recovery		
	Mean	Std. dev.	% CV	Mean	Std. dev.	% CV
1A-1B	69.9	5.41	7.7	69.2	17.2	24.9
1C-1D	65.8	1.57	2.4	71.2	2.12	3.0
2A-2B	88.8	8.00	9.0	152.2	45.7	30.0
2C-2D	61.2	9.59	15.7	72.0	26.4	36.7
3A-3C	80.8	1.86	2.3	92.6	1.85	2.0
3B-3D	93.7	1.76	1.9	100.2	0.40	0.4
4A-4C	102.6	2.86	2.8	102.2	3.60	3.5
4B-4D*	-	-	-	-	-	-
5A-5C	114.0	44.8	39.3	127.6	1.30	1.0
5B-5D	94.7	2.25	2.4	107.7	4.28	4.0
Pooled						
(a)†	85.7	15.7	18.3	99.4	18.6	18.7
(b)§	87.5	17.4	19.9	96.2	10.3	10.7

* Deleted because of sampling problems.

† Pooled (a) values include all run pairs except 4B-4D.

§ Pooled (b) values do not include 1A-1B, 2A-2B, or 4B-4D.

The standard deviations in Column 2 were tested for homogeneity of variance by the Bartlett test and were found not to be homogeneous. Specifically the standard deviation of run pair 5A-5C equal to 44.8 might not be considered as part of a uniform population of standard deviations. This value might be declared to be an outlier and discarded from the data set, except for the fact that when corrected for the deuterated spike, it appears to fall into line with the standard deviations in Column 5 of the table. It is, therefore, not recommended that the value be deleted from the data set as an outlier.

The standard deviations of Column 2 were pooled by the following formula:

$$s_{pooled} = (s^2_{1C-1D} + s^2_{2C-2D} + s^2_{3A-3C} + s^2_{3B-3D} +$$
$$s^2_{4A-4C} + s^2_{5A-5C} + s^2_{5B-5D})/7)^{\frac{1}{2}}$$

The pooled means were calculated as the arithmetic mean of the mean values. The overall precision in terms of percent coefficient of variation is calculated by:

$$\% \text{ CV} = (s_{pooled}/\bar{\bar{X}}) \times 100$$
$$= (17.4/87.5) \times 100$$
$$\% \text{ CV} = 19.9 \text{ percent precision}$$

The overall variance for the field study includes the sampling variance, the sample preparation variance, and the analytical variance as follows:

$$\text{Overall } s^2 = s^2_G + s^2_p + s^2_A$$

For the field tests: $\bar{X} = 26.85$ ng/μL

Using the MDL calibration

$@\ \bar{X} = 26.85$ ng/μL, $\hat{Y} = 19{,}704$

$s = 0.199 \times 19{,}704 = 3{,}795.7$

@ X = 26.85, % CV for GC/MS = 8.924 (see Table D-3)

$s_A = 0.08924 \times 19{,}704 = 1{,}702.2$

$s_p = \sqrt{\frac{(1702.2)^2\ (6.41)}{93.59}} = 445.5$

$s_G^2 = 11{,}318{,}357$

$s_G = 3{,}364.3$

Calculate percent of total variance for sampling, preparation, and analytical steps.

$$\text{Sampling:}\quad \%\ \text{CV} = \frac{3{,}364.3}{19{,}704} \times 100 = 17.1 \text{ percent}$$

$$\text{Preparation:}\quad \%\ \text{CV} = \frac{445.5}{19{,}704} = 2.3 \text{ percent}$$

$$\text{Analysis:}\quad \%\ \text{CV} = \frac{1{,}702.2}{19{,}204} = 8.6 \text{ percent}$$

These % CV values characterize to some extent the precision of each step in the procedure.

APPENDIX E

FIELD TEST PROGRAM

Appendix E presents a description of the field testing portion of this program to evaluate the bias and precision of the Semi-VOST method. Included in this appendix are descriptions of the test site, the sampling equipment and sample plan, and a listing of the raw data collected in the field. Sample collection procedures and protocols were presented in Appendix A. An analysis of the field test results is presented in Appendix F and summarized in Chapter 6 of the final report.

TEST SITE DESCRIPTION

Trade Waste Incineration, a division of Chemical Waste Management Inc., operates a hazardous waste incinerator at Sauget, Illinois. The purpose of this incinerator is to destroy hazardous industrial waste other than PCBs and dioxins by combustion at elevated temperatures. The waste streams incinerated are:

1. liquid high Btu - containing mostly waste organic solvents,
2. liquid low Btu - containing water-soluble organic solvents (40 percent organics),
3. slurries and sludges - containing primarily organic sludges and slurries, and
4. solids - containing almost any hazardous material in solid form.

These wastes are injected into the incinerator at varying times to be combusted. The temperature of the incinerator is maintained in the 982-1093°C range. If the feed of one source has insufficient Btu content to maintain this temperature or if a waste stream with too high a Btu content is fed, the operator can switch feed or discontinue feed to allow for a smooth operation.

The process is required to maintain combustion conditions such that the CO emissions are kept below the 50 ppmv threshold level. Both temperature and CO monitors allow the operator to change feeds accordingly.

Figure E-1 is a block diagram of the incinerator process and the control devices. The waste is fed into the primary combustion chamber where it is volatilized and partially combusted at ∼982°C. From there, the gaseous stream enters the secondary chamber where the temperature is maintained at ∼1093°C with auxiliary fuel. The overall retention time for both chambers is ∼5 seconds. The gaseous combustion products exit the combustion chamber and pass through a venturi scrubber, a packed scrubber where ammonia is added to neutralize the hydrochloric acid, a large liquid demister containing coalescing filter pads, and finally exhaust through the stack.

When the incinerator is operated at optimal conditions, the high Btu stream is fed at 5.4 kg per minute and the low Btu stream at 6.8 kg per minute. The slurry stream feed rate is consistent at approximately 4.5 kg per minute. During the field sampling, when solids were fed to the incinerator, the operator stopped the flow of the high Btu and low Btu feeds for approximately 1 minute. After that period, the flow of the low and high Btu streams was reinstated. During this Semi-VOST evaluation study, a normal load was approximately 18 kg of solids every 5 minutes. The solid waste feed to the incinerator during this test period was comprised of hospital waste, vermiculite, rags, and solid materials. Occasionally, waste sulfuric acid was fed although only in small amounts so the ammonia scrubber system would not be overloaded. In addition, small amounts of outdated nitroglycerin tablets were added to most of the solids during Runs 4 and 5.

During Runs 4 and 5, hexachlorocyclopentadiene (C-5,6) was spiked into the high Btu waste stream at approximately 1 percent (weight basis) of the total feed. The level of spiking was determined by taking the maximum feed rates for each stream and calculating the pounds per minute required to give a 1 percent feed rate. During Run 3, the high Btu feed was spiked with dibromomethane at the 1 percent level. During Runs 1 and 2, there was no low Btu stream being fed. The low Btu waste became

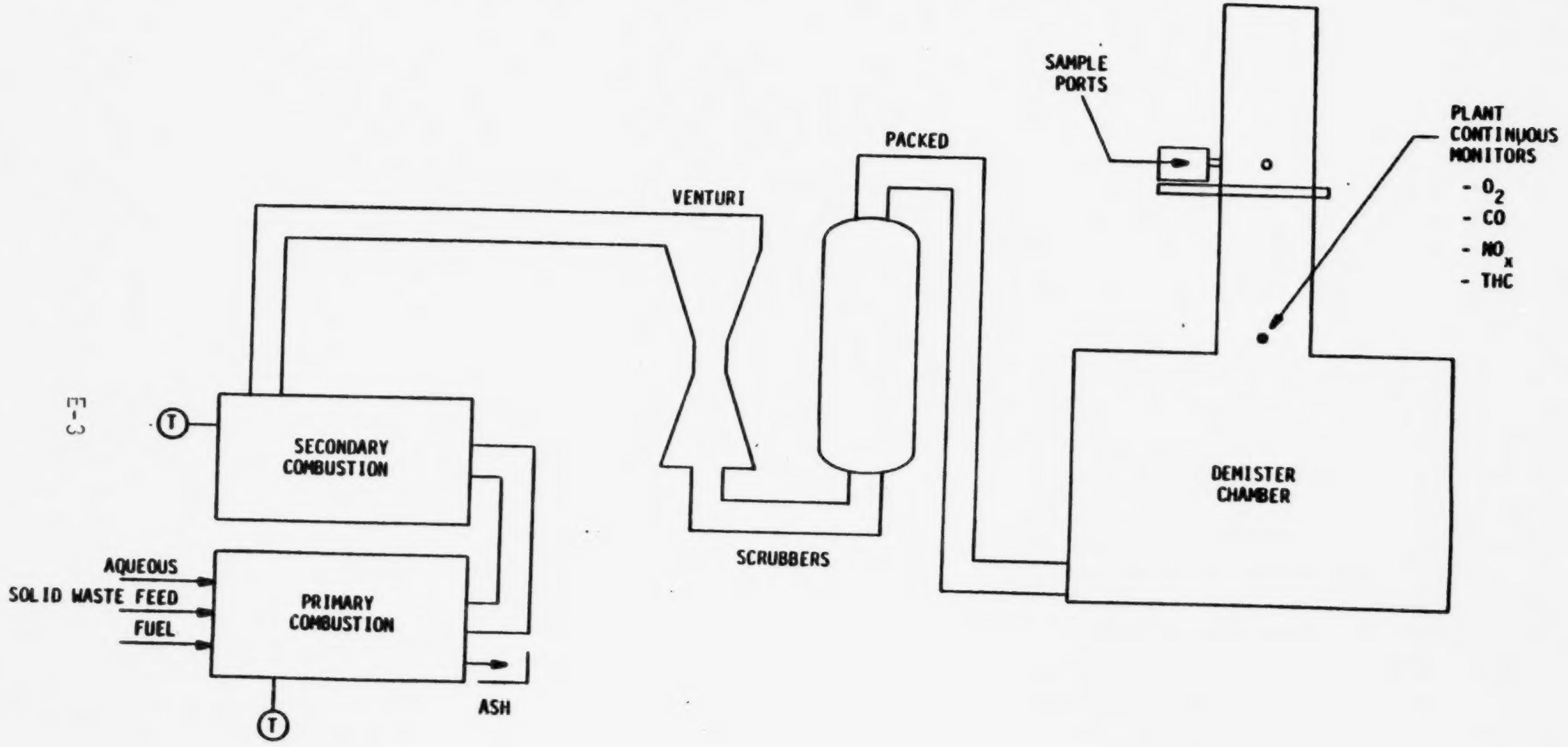

SAMPLE PORTS
PACKED
PLANT CONTINUOUS MONITORS
- O_2
- CO
- NO_x
- THC
VENTURI
SECONDARY COMBUSTION
DEMISTER CHAMBER
SCRUBBERS
AQUEOUS
SOLID WASTE FEED
FUEL
PRIMARY COMBUSTION
T
T
ASH

Figure E-1. Trade Waste Incineration incinerator configuration.

available for subsequent runs. The sludge, high Btu waste, and the solids were fed continuously throughout Runs 1 through 5. The feed composition of the waste as supplied by Trade Waste Incineration is given in Table E-1.

Environmental and Plant Conditions During the Test

The tests were conducted during the weeks of February 3 and February 10, 1985. The weather conditions at the plant were extremely adverse. At no time during the testing period did the ambient temperature exceed freezing (0°C). Quite often the wind chill index was below -18°C and went down to -30°C at one point. These conditions provided the worst possible case both for the process and for the sampling. The extreme cold could have been responsible for the partial plugging of the primary chamber exhaust during the first and second runs. The plug was removed the following day along with the clinkers in the primary chamber.

The only other process condition of note was that the sampling stream was supersaturated with water. Water droplets were noticed in the stack during each of the runs, possibly due to the extremely cold temperatures.

SAMPLING EQUIPMENT DESCRIPTION

Each test run was performed with four separate Semi-VOST trains as shown in Figure E-2. Each separate train contained every train component element shown with the exception of the pitot tube and the thermocouple. In order to obtain identical samples of the exhaust stream for each of the trains, a common probe system was used to accommodate all four train systems (quad probe). The quad probe contained four separate probes and nozzles but only two pitot tubes for flow measurements and two thermocouples for temperature measurements. Figure E-3 is a diagram of this quad probe.

Each test series was performed with four trains operating at a single point in the stack. The sampling point chosen was a point of average velocity which was approximately 10.2 cm into the stack. Each train was run isokinetically using the pitot measurements of the pitot closest to the two probes in the stack. For example, the left side of

TABLE E-1. WASTE FEED COMPOSITION

High Btu feed*	Low Btu feed*	Sludge	Solids
Feed rate = 5.4 kg/min	6.8 kg/min	4.5 kg/min	4.5 kg/min
Composition			
Toluene - 4.88 percent 1,1,1-trichloroethane - 10 percent Xylene - 10 percent Isopropyl chloride Glycols Pesticide wastes Cement wastes Paint/ink wastes Various solvents Various chlorinated organics Various organic mixtures	Pesticide manufacturing wastes - 1 percent pesticides in aqueous solution	NA†	NA

* These mixtures were fed from a single tank.

† NA = not available.

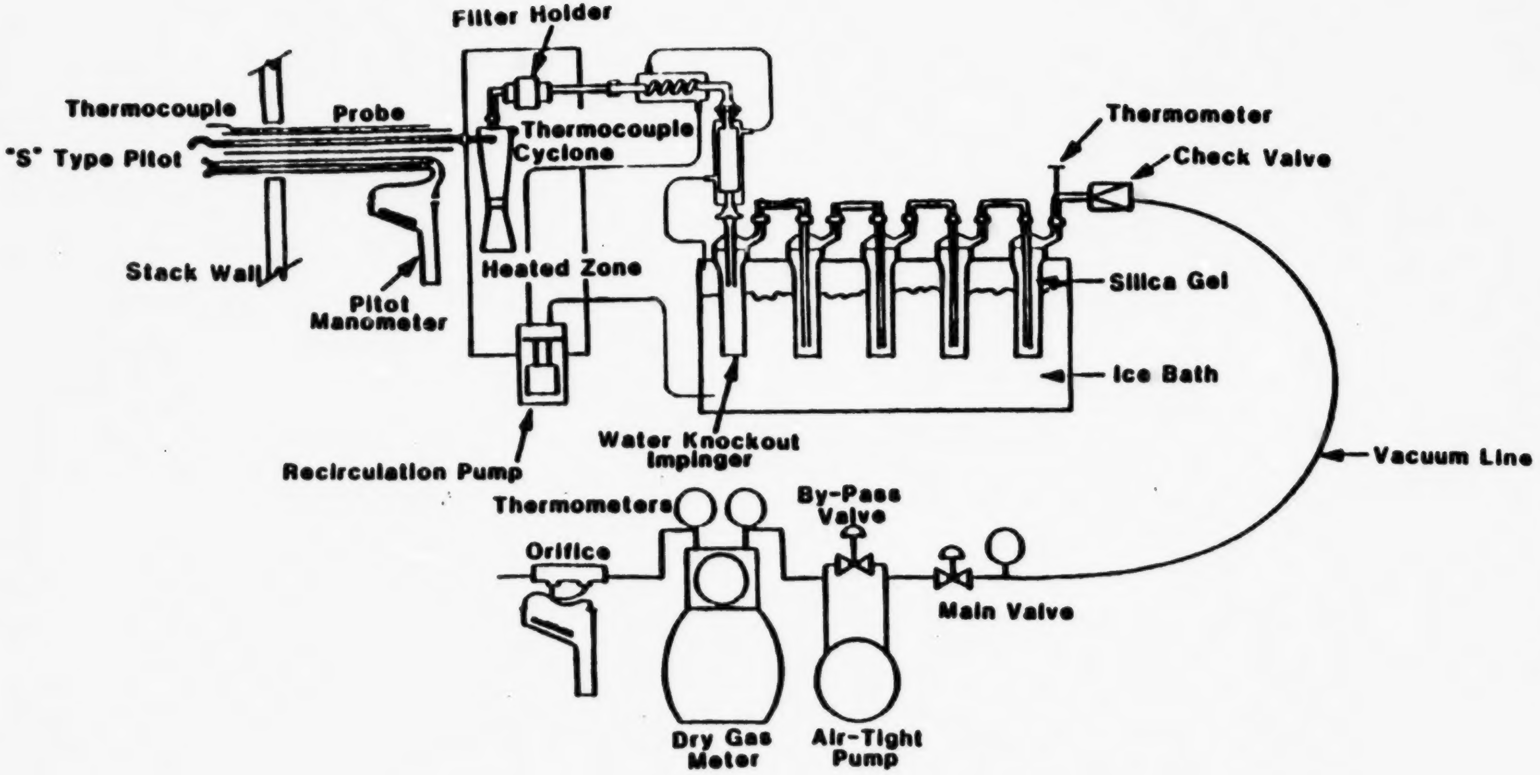

Thermocouple
"S" Type Pitot
Stack Wall
Probe
Pitot Manometer
Filter Holder
Thermocouple
Cyclone
Heated Zone
Recirculation Pump
Water Knockout Impinger
Thermometer
Check Valve
Silica Gel
Ice Bath
Vacuum Line
Thermometers
Orifice
By-Pass Valve
Main Valve
Dry Gas Meter
Air-Tight Pump

Figure E-2. Semi-VOST train.

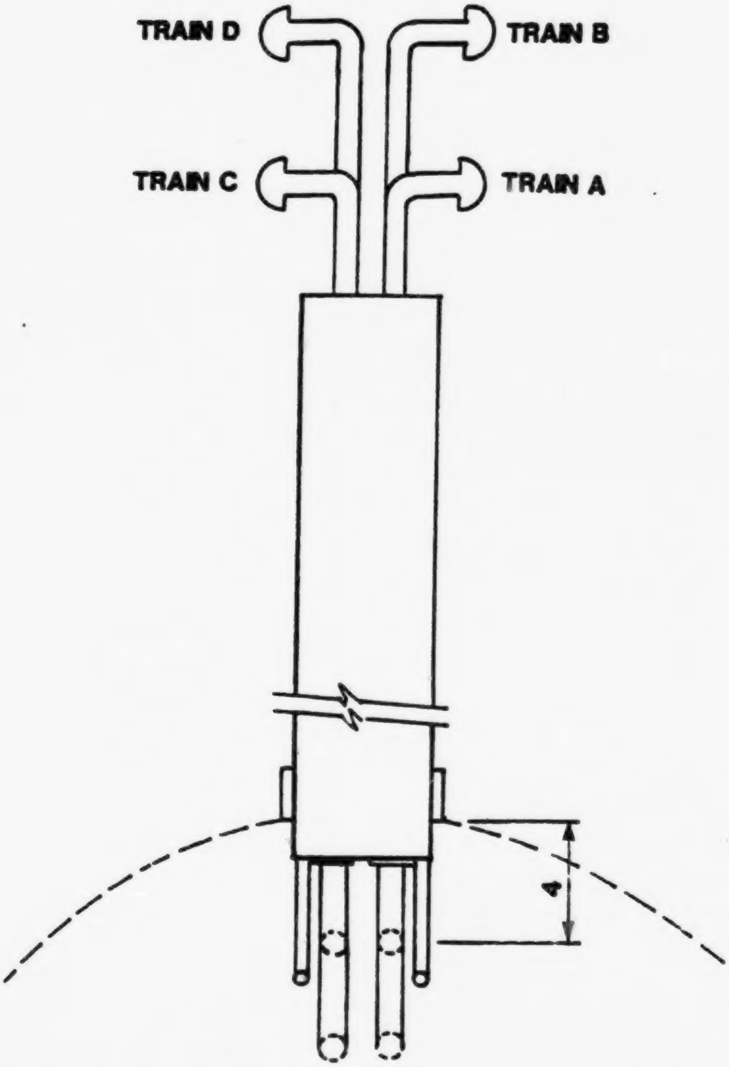

TRAIN D
TRAIN B
TRAIN C
TRAIN A
4

Figure E-3. Quad probe.

the quad probe utilized temperature and flow measurements from the left pitot and thermocouple while the right side utilized the right pitot and thermocouple.

A dynamic spiking system was located on the sampling platform. This system consisted of compressed gas cylinders, regulators, heated lines, mass flow controllers, and glass injection "T's." Figure E-4 shows the spiking apparatus that was used. Both the sampling trains and the spiking equipment were located on a common sampling platform. The entire platform was covered and heated to provide an ambient temperature of approximately 7.2°C.

Semi-VOST Trains

There was no deviation from the method or test plan relative to the train set-up. The probe and filter temperatures were maintained at 121°C as specified in the test plan. With the exception of the specially designed quad probe, the trains were the standard EPA Method 5 trains with a condenser and XAD-2® resin trap added to meet the specifications of Semi-VOST. The probe liners were modified with right angle bends at the ball joint end to facilitate connection to the filter boxes of each train. Trains A and C had shorter probe lengths than Trains B and D. The sampling nozzles conformed to EPA design. However, the nozzles for Trains A and C were shorter than the nozzles for Trains B and D to ensure that all sampling took place on the same plane with no flow disturbances (see Figure E-5).

Spiking Apparatus

The dynamic spiking of the sampling trains with toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane was accomplished utilizing the apparatus shown in Figure E-4. This system was comprised of five flow controllers, two readout devices, and interconnecting tubing. Flow controllers FC-1, FC-2, and FC-3 were delivering preset flows of 88, 13, and 5 cc/min, respectively, for toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane, from compressed gas cylinders. The three gases were mixed at a common point and the stream was split and then directed to flow controllers FC-4 and FC-5. These two flow controllers were set to

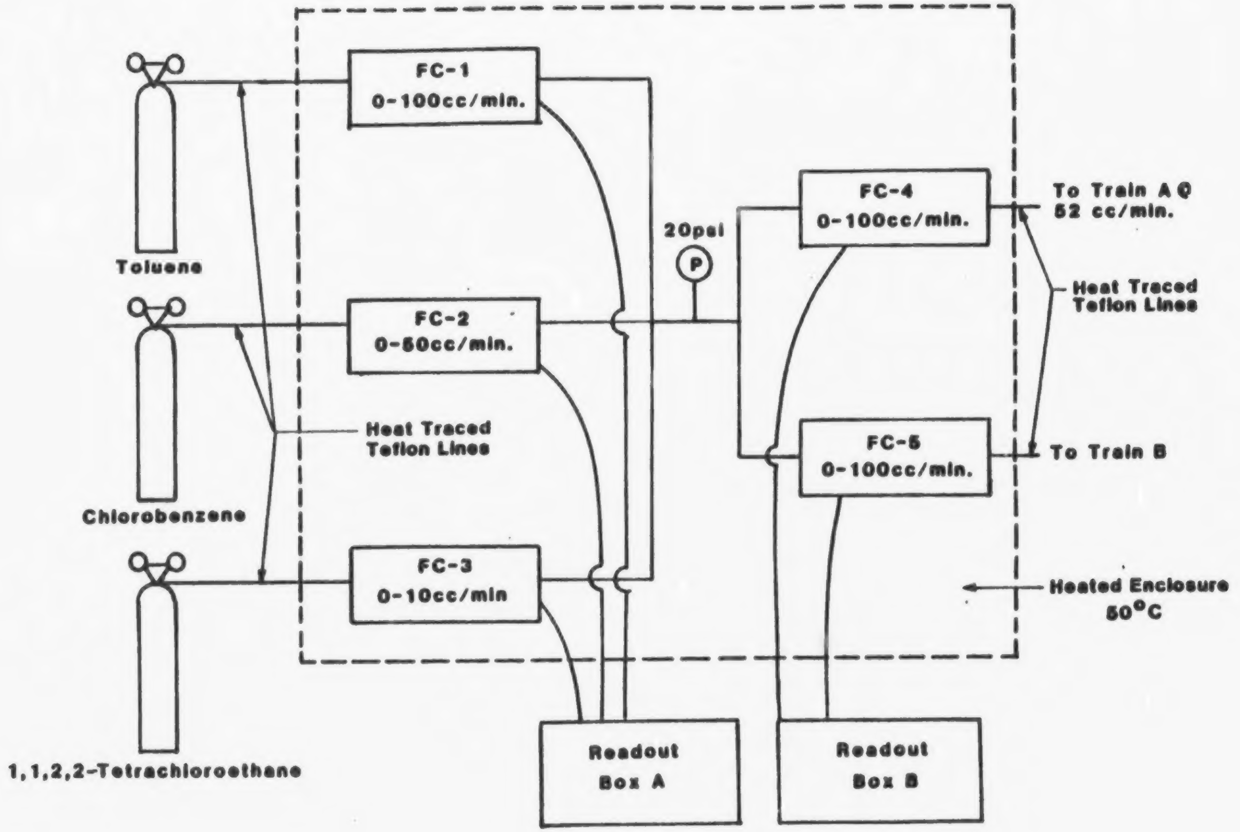
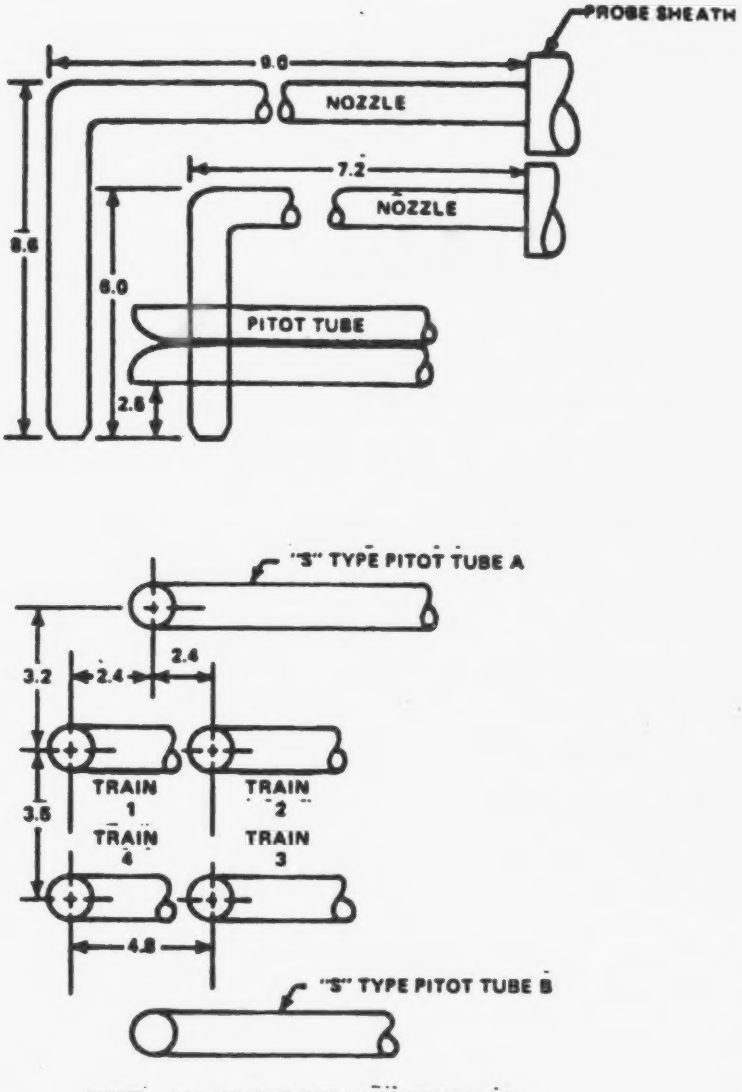

FC-1
0-100cc/min.
FC-2
0-50cc/min.
FC-3
0-10cc/min
FC-4
0-100cc/min.
FC-5
0-100cc/min.
20psi
P
Toluene
Chlorobenzene
1,1,2,2-Tetrachloroethane
Heat Traced
Teflon Lines
To Train A @
52 cc/min.
Heat Traced
Teflon Lines
To Train B
Heated Enclosure
50°C
Readout
Box A
Readout
Box B

Figure E-4. Dynamic spiking apparatus.


PROBE SHEATH
9.0
NOZZLE
7.2
NOZZLE
8.6
6.0
PITOT TUBE
2.6
"S" TYPE PITOT TUBE A
3.2
2.4
2.4
TRAIN 1
TRAIN 2
3.6
TRAIN 4
TRAIN 3
4.8
"S" TYPE PITOT TUBE B

NOTE – ALL DIMENSIONS IN CENTIMETERS

Figure 4-5. Double pitot sampling arrangement: (top) side view; (bottom) upstream view.

deliver 52 cc/min each to Trains A and B during Runs 1 and 2. The gaseous spike entered each train through a glass "T" located after the filter and before the condenser of each train. The Teflon® lines leading from the gas cylinders to the flow controllers and from the controllers to the glass "T" were heat-traced and maintained at approximately 120°C. The flow controller assembly was enclosed and maintained at approximately 50°C. For proper operation, each flow controller required a minimum pressure drop of 1.4 kg/cm^2 (20 psig). The pressure exiting the gas cylinders was maintained at 2.8 kg/cm^2 (40 psig) (above ambient). The pressure prior to FC-4 and FC-5 was 1.4 kg/cm^2 (20 psig), with the exiting gas entering the sampling trains at ambient pressure. Under the preset conditions of pressure and flow, equal volumes of the spiking gas mixture were delivered to the specified sampling trains during the entire sampling period.

The spiking apparatus described above was calibrated and tested in the laboratory prior to this field testing. Flow controllers FC-1, FC-2, and FC-3 were calibrated at 2.8 kg/cm^2 (40 psig) and controllers FC-4 and FC-5 were calibrated at 1.4 kg/cm^2 (20 psig). The results of the preliminary laboratory tests showed that the spiking system required a finite equilibration time before accurate compound delivery could be expected. The optimal time was found to be approximately 2 hours. The minimum equilibration time allowed during these tests was 4 hours.

Field Staging Area

The host plant provided a room for on-site calibration, train preparation, and recovery. One side of the room was used for sample preparation, sample recovery, sample custody, and packaging for shipment to the RTP laboratory. The other side of the room was set up with a GC/FID and a computerized integrating recorder. These instruments were used to calibrate the spiking system prior to and after the spiking tests at the stack. In addition to the GC/FID, a soap film flow meter was set up to check the flows of the mass flow controllers prior to testing.

The staging area was located away from the waste storage area and the analytical laboratory so that possible contamination from external sources in the recovery area was minimized.

"Blank" Trains

A complete train was assembled to serve as a blank for each test. The components of this additional train were chosen at random from the sets of glassware that were shipped to the site. Each piece was assembled in the set-up/recovery area. The complete set of glassware was then transported to the test location with the other glassware and leak-checked at the stack. Following the test, the blank train was leak-checked again and returned to the recovery area where it was disassembled along with the test trains. The series of blanks collected in this manner were called "Train" blanks. Other blanks taken were "Trip" blanks which accompanied the equipment during transportation but were not loaded into a train. These blanks were stored in the staging area.

SAMPLING SCHEDULE

The field test consisted of a series of five runs which were taken on 3 test days. Each test run had four trains (A, B, C, D) connected to the quad probe. The quad probe nozzles sampled from a single point in the stack that was representative of average velocity. During Tests 1 and 2, Trains A and B were spiked with 10 times the minimum detectable level of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane. The calculations for the amount spiked are the same as for the pretest checkout of the spiking apparatus. Runs 3, 4, and 5 were distributive volume experiments in which Trains A and C were operated for one-half the time of Trains B and D. During Run 3, the time period consisted of 2 hours for Trains A and C and 4 hours for Trains B and D. Runs 4 and 5 were shortened to runs of 1 hour and 2 hours due to plant constraints. Table E-2 presents the testing schedule along with the test parameters for the 5-day test period.

Table E-2. TEST PARAMETERS AND SCHEDULE

TEST PARAMETERS

	Trains A, B	Trains C, D	
Run 1 -	Spiked with 3 organics (toluene, chlorobenzene, 1,1,2,2-tetrachloroethane)	Unspiked	2 h - colocated probes; 0.014 m^3 (0.5 cfm) single point
Run 2 -	Spiked with 3 organics (toluene, chlorobenzene, 1,1,2,2-tetrachloroethane)	Unspiked	2 h - colocated probes; 0.014 m^3 (0.5 cfm) single point
	Trains A, C	Trains B, D	
Run 3 -	2 h run	4 h run	0.5 cfm single point colocated probes; 2 filters required for each train
Run 4 -	1 h run	2 h run	0.5 cfm single point colocated probes
Run 5 -	1 h run	2 h run	0.5 cfm single point colocated probes

TEST SCHEDULE

Day 1 - Set up
Day 2 - Runs 1 and 2 (spiking runs)
Day 3 - Recovery (temperature - 22°F, clinkers removed from exhaust)
Day 4 - Run 3, 2 h/4 h distributive volume run
Day 5 - Recovery
Day 6 - Runs 4 and 5 (1 h/2 h distributive volume run)
Day 7 - Recovery/pack
Day 8 - Travel

APPENDIX F
FIELD TEST ANALYTICAL DATA

GC/MS CALIBRATION/INSTRUMENT CONDITIONS

Extracted samples were analyzed on a Finnigan 5100 gas chromatograph/mass spectrometer/data system. Operating conditions are shown in Table F-1. Decafluorotriphenylphosphine (DFTPP) was used to establish tuning criteria according to Table F-2. A Supelco column performance mixture containing octanone, decane, 1-octanol, undecane, 2,6-dimethylphenol, 2,6-dimethylaniline, naphthalene, dodecane, and tridecane was used weekly to monitor acceptability of column performance. Column performance data are reported in Appendix G. A five-point calibration curve was prepared in triplicate.

The concentration levels for surrogate compounds (d_8-1,4-dioxane, d_5-pyridine, d_8-toluene, d_5-chlorobenzene, d_5-phenol, d_5-nitrobenzene, d_8-naphthalene, and $^{13}C_6$-pentachlorophenol) and target compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) were 10, 25, 50, 100 and 200 ng/uL. The quantitation standard, d_{10}-phenanthrene, was held constant at 100 ng/uL. For some of the compounds, the entire range of calibration standards did not produce points which could be used to generate a calibration curve because of saturation of the ions of the compounds at the higher concentration levels. A fifteen-point calibration curve requires approximately two days to generate. Data for a five-point calibration curve (a single injection at each concentration level) and the fifteen-point calibration (triplicate injections at each concentration level) are shown in Table F-3. Values obtained for calibration samples analyzed twice daily and control charts are shown in the Quality Control Section (Appendix G). The five-point calibration can be generated in one day of analysis, and the relative percent difference between the five-point and the fifteen-point calibration values exhibits a small change. The additional replicates do often improve the precision of the

Table F-1. OPERATING CONDITIONS GC/MS ANALYSIS OF EXTRACTED SAMPLES

Instrument	Finnigan 5100 Gas Chromatograph/Mass Spectrometer/Data System
Column	30m wide-bore (0.32 mm) thick film (1 u) DB-5 fused silica capillary
Carrier gas	Helium
Split flow	15 mL/min
Septum sweep	3 mL/min
Column head pressure	(0.8 kg/cm^2) 10.8 psi
Injector temperature	300°C
Transfer line oven	270°C
Injection conditions	Splitless 0.6 min, then split
GC temperature program	40°C for 4 min, then 10°C/min to 270°C and hold for 20 min
Electron energy	70eV, nominal
Ionization conditions	Electron ionization
Mass range	35-500 daltons
Scan cycle	1 sec

TABLE F-2. DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z Abundance criteria*
51	30-60 percent of mass 198
68	Less than 2 percent of mass 69
70	Less than 2 percent of mass 69
127	40-60 percent of mass 198
197	Less than 1 percent of mass 198
198	Base peak, 100 percent relative abundance
275	10-30 percent of mass 198
365	Greater than 1 percent of mass 198
441	Present but less than mass 443
442	Greater than 40 percent of mass 198
443	17-23 percent of mass 442

* Federal Register, Vol. 49, No. 209, Friday, October 26, 1984.

TABLE F-3. CALIBRATION CURVES FOR QUANTITATIVE ANALYSIS

		5 Points			15 Points			
Compound	Ion	Mean response factor	Standard deviation	Coefficient of variation	Mean response factor	Standard deviation	Coefficient of variation	Relative percent difference*
d_{10}-phenanthrene	160	1.000	0	0	1.000	0	0	--
	188#	--	--	--	--	--	--	--
d_8-1,4-dioxane	62	0.437	0.027	6.1	0.472	0.029	6.1	7.4
	96	1.268	0.105	8.3	1.359	0.088	6.5	6.7
d_5-pyridine	52	1.339	0.058	4.3	1.426	0.076	5.3	6.1
	84	3.280**	0.136	4.1	--	--	--	--
d_8-toluene	54	0.839	0.056	6.6	0.899	0.052	5.8	6.7
	70	0.949	0.053	5.5	1.025	0.058	5.6	7.4
	98	5.591**	0.188	3.4	--	--	--	--
d_5-chlorobenzene	54	1.701	0.213	12.5	1.851	0.114	6.2	8.1
	117	4.181**	0.179	4.3	4.345**	0.250	5.8	3.8
	119	1.263	0.141	11.2	1.374	0.079	5.7	8.1
d_5-phenol	71	1.675	0.370	22.1	1.819	0.149	8.2	7.9
	99	3.866**	0.509	13.2	3.730**	0.364	9.8	3.6
d_5-nitrobenzene	98	0.388	0.013	3.2	0.409	0.030	7.2	5.1
	128	1.057	0.092	8.7	1.102	0.137	12.4	4.1
d_8-naphthalene	108	1.049	0.170	16.2	1.124	0.071	6.3	6.7
	136	7.97**	1.385	17.4	8.329##	1.374	16.5	4.3
$^{13}C_6$-pentachlorophenol	270	0.306	0.045	14.8	0.311	0.050	16.2	1.6
	272	0.490	0.059	12.0	0.499	0.077	15.4	1.8
toluene	51	0.816	0.075	9.2	0.858	0.058	6.8	4.9
	65	1.193	0.074	6.2	1.279	0.068	5.3	6.7
	91	6.744**	0.271	4.0	7.012**	0.381	5.4	3.8
chlorobenzene	51	1.621	0.215	13.2	1.771	0.112	6.4	8.5
	112	4.094**	0.181	4.4	4.229**	0.220	5.2	3.2
	114	1.217	0.132	10.8	1.329	0.072	5.4	8.4
1,1,2,2-tetrachloroethane	83	4.078**	0.409	10.0	4.274	0.386	9.1	4.6
	131	0.294	0.033	11.3	0.310	0.019	6.0	5.2
	168	0.186	0.023	12.1	0.199	0.012	6.2	6.5

* Calculated as $\frac{RF_5 - RF_{15}}{RF_{15}}$ where RF_5 = mean value for five data points and RF_{15} = mean value for 15 data points.

# Molecular ion (m/z 188) of d_{10}-phenanthrene saturated at 100 ng/uL so a fragment ion (m/z 160) was used.

** The ion was saturated at 100 and 200 ng/uL, so the mean represents 10, 25, and 50 ng/uL for this ion only. Other ions for the compound provided usable values through the entire concentration range.

## Eight usable data points.

determination, as illustrated by the change in the percent coefficient of variation exhibited by the ions of d_5-phenol (22.1 vs. 8.2 and 13.2 vs. 9.8) but the improvement is not a consistent trend for all ions of all compounds. The mean values from the fifteen-point calibration data base were used to generate quantitative information and to check daily values, but the additional time and effort required to generate five triplicate points at each concentration level do not appear to be warranted by either the change in the values obtained or the precision of measurement observed in each case. Since the precision of measurement, as illustrated by the coefficient of variation, was less than 20 percent for all of the response factors for the compounds of interest, a mean value for the response factor was used in quantitative calculations and regression analysis was not used to generate a calibration curve.

SELECTION OF OTHER COMPOUNDS FOR QUANTITATION

Qualitative analysis was performed on five of the XAD-2® extracts in order to assess what additional compounds, other than the 3 targets, could be selected to study the effect of the distributive air volumes. The instrument was not calibrated for compounds other than the deuterated surrogates and the spiked target compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane). Therefore, in order to obtain estimated quantities of the additional compounds, a relative response factor of 1 (relative to the analytical standard, d_{10}-phenanthrene) was assumed. The following equations were used for quantitation:

$$\text{Relative Response Factor} = \frac{A_{cpd}/ng_{cpd}}{A_{std}/ng_{std}}$$

where:

A_{cpd} = system response for the compound of interest

A_{std} = system response for the quantitation standard

ng_{cpd} = nanograms of compound of interest injected

ng_{std} = nanograms of standard injected then:

$$ng_{cpd} = \frac{A_{cpd} \cdot ng_{std}}{A_{std} \cdot RRF}$$

The compounds selected to follow distributive air volumes were 4-methyl-2-pentanol, benzoic acid, benzoyl chloride, $C_{16}H_{33}CHO$, and diisooctyl phthalate. These compounds were selected because they were present in the XAD-2® extracts that were characterized and thus would possibly be present in varying amounts as a function of the volume of gas sampled. The results calculated for these compounds (assuming a relative response factor of 1) are shown in Tables F-4 and F-5. Using these compounds to illustrate variation in concentration as a function of volume of gas samples does not, in general, appear to be correct. Values for some of the compounds are observed to be higher in some of the blanks than in some of the samples, and the compounds do not exhibit even an approximate doubling in concentration when the volume of gas sampled doubles. A different choice of compounds may possibly better illustrate a change in concentration with change in sampled volume, but qualitative and quantitative characterization of more of the samples would be required. However, the change or lack of change in concentration with gas volume sampled with this particular selection of compounds does raise some interesting questions. Since these compounds are observed in XAD-2® extracts and extracts of media other than XAD-2® for actual samples and blanks, their presence may be due to artifact formation. Other than benzoyl chloride, which is usually present in low amounts, all of the other compounds are usually present in the extracts in substantial quantities. Granted that the quantitative values calculated are only estimates based on the assumption of a value of 1 for the relative response factor, a comparison of the relative sizes of the peaks in the chromatograms indicates that fairly extensive formation of these compounds must be occurring.

Qualitative analysis was performed with the aid of a computerized library search on the INCOS data system. Compounds observed are shown in Table F-6, which is presented in two parts. In Part 1, compounds which

TABLE F-4. COMPARISON OF RESULTS BY SAMPLE TYPE FOR PROBE RINSE, COIL RINSE, CONDENSATE/RINSE, AND IMPINGER/RINSE

Compound	Probe rinse			Coil rinse			Condensate and rinse		
	Blank-1	1-A*	1-B*	Blank-1	1-A*	1-B*	Blank-1	1-A*	1-B*
Surrogate compounds, % recovery									
d_8-1,4-dioxane	90	110	84	121	75	65	81	77	71
d_5-pyridine	100	118	86	118	80	64	74	71	58
d_8-toluene	92	109	91	70	72	61	84	41	39
d_5-chlorobenzene	97	116	92	118	80	67	90	68	53
d_5-phenol	106	115	87	112	86	71	97	87	75
d_8-nitrobenzene	113	140	97	110	94	70	137	106	90
d_8-naphthalene	105	131	101	78	97	82	114	89	84
$^{13}C_6$-pentachlorophenol	79	143	84	112	84	68	116	38	30
Target compounds, ng/ul									
toluene	3.1	9.2	7.0	3.0	3.6	3.2	4.0	NF#	NF
chlorobenzene	NF	NF	NF	NF	NF	NF	NF	NF	NF
1,1,2,2-tetrachloroethane	NF	NF	NF	NF	NF	NF	NF	NF	0.4
Other Compounds, ng/ul									
4-methyl-2-pentanol	NF	NF	NF	NF	NF	NF	4.6	3.6	NF
benzoic acid	4.9	7.0	NF	0.5	1.2	NF	NF	8.6	1.4
benzoyl chloride	NF	NF	NF	NF	NF	NF	NF	NF	NF
$C_{16}H_{33}CHO$	410	33.4	7.2	13.2	141	240	314	522	708
Diisooctyl phthalate	5.8	7.4	4.2	3.7	3.8	3.4	8.0	17.6	16.0
Sample Volume (dscf)	0	63.6	67.3	0	63.6	67.3	0	63.6	67.3

(continued)

TABLE F-4. (Continued)

	Impinger and rinse									
	Blank-1**	1-A*	1-B*	2-A*	2-B*	3-C	3-D	Mean	SD	% CV
Surrogate compounds, % Recovery										
d_8-1,4-dioxane	61	79	122	76	101	82	71	85.4	18.7	21.9
d_5-pyridine	67	77	114	85	98	82	77	85.6	18.9	22.1
d_8-toluene	41	69	91	40	50	45	27	63.9	24.5	38.3
d_5-chlorobenzene	49	76	105	58	64	57	44	77.1	23.6	30.6
d_5-phenol	76	78	109	84	105	87	78	90.8	14.5	15.9
d_8-nitrobenzene	86	102	156	98	138	118	103	109.9	22.9	20.9
d_8-naphthalene	72	91	122	94	106	94	75	95.9	16.7	17.4
$^{13}C_6$-pentachlorophenol	314	150	105	111	91	189	169	117.7	67.9	57.7
Target compounds, ng/uL										
Toluene	NF	NF	NF	NF	NF	NF	NF			
Chlorobenzene	NF	NF	NF	NF	NF	NF	NF			
1,1,2,2-tetrachloroethane	NF	NF	NF	NF	NF	NF	NF			
Other compounds, ng/uL										
4-methyl-2-pentanol	NF	2.4	NF	NF	NF	4.8	17.6			
benzoic acid	11.1	4.0	4.3	1.0	2.4	13.6	14.8			
Benzoyl chloride	NF	NF	NF	NF	NF	NF	NF			
$C_{16}H_{33}CHO$	27.2	54.4	16.7	12.8	31.7	18.4	82.2			
diisooctyl phthalate	2.9	3.6	3.8	4.4	9.4	6.6	116.6			
Sample Volume (dscf)	0.0	63.6	67.3	64.5	63.5	53.3	94.9			

* Field spike.

# NF - not found.

** Mean of three replicates.

TABLE F-5. COMPARISON OF RESULTS BY SAMPLE TYPE FOR ALL XAD-2® TRAPS

	Run #1					Run #2				Run #3			
Compound	Blank-1	1-A*	1-B*	1-C	1-D	2-A*	2-B*	2-C	2-D	3-A	3-B	3-C	3-D
Surrogate compounds						% Recoveries							
d_8-1,4-dioxane	87	113	92	86	84	78	72	97	73	76	95	85	90
d_5-pyridine	92	103	85	91	87	78	74	91	74	60	51	16	58
d_8-toluene	81	104	89	92	81	77	75	87	65	68	92	79	80
d_5-chlorobenzene	89	116	91	96	89	79	82	102	75	79	92	90	95
d_5-phenol	101	119	102	105	95	92	86	115	89	84	107	94	101
d_5-nitrobenzene	107	150	141	115	108	102	120	148	103	110	128	128	134
d_8-naphthalene	102	136	120	113	98	98	98	127	101	102	122	106	111
$^{13}C_6$-pentachlorophenol	39	124	216	121	126	176	185	87	113	176	134	186	168
Target compounds, ng/uL													
toluene	NF#	10.1	17.4	2.4	2.0	16.0	20.4	NF	NF	2.0	7.3	2.6	7.0
chlorobenzene	0.1	23.8	28.0	26.1	22.6	34.7	60.1	20.3	20.8	23.6	53.9	24.8	51.0
1,1,2,2-tetrachloroethane	NF	1.8	2.0	NF	NF	1.4	1.2	NF	NF	NF	NF	NF	NF
Other compounds, ng/uL													
4-methyl-2-pentanol	3.6	83.0	135	74.2	53.8	282	143	150	137	248	291	318	270
benzoic acid	33.0	76.0	120	77.0	80.6	92.0	91.0	95.7	98.6	330	370	559	352
benzoyl chloride	56.4	16.9	35.6	19.2	17.0	36.0	31.5	21.1	22.8	22.2	21.5	21.6	24.8
$C_{16}H_{33}CHO$	40.8	241	6.2	12.1	5.6	2.0	11.0	12.7	16.6	26.0	16.3	15.8	23.8
diisooctyl phthalate	56.6	53.0	37.6	24.1	33.0	16.0	13.0	36.0	25.0	6.8	19.0	9.6	6.8
Sample Volume (dscf)	0.0	63.6	67.3	68.6	61.4	64.5	70.0	65.6	53.8	52.4	103	53.3	94.9

TABLE F-5. (Continued)

	Run #4						Run #5						
	Blank-3	4-A	4-B	4-C	4-D	4-D**	5-A	5-B	5-C	5-D	Mean	SD	% CV
Surrogate compounds, % recoveries													
d_8-1,4-dioxane	81	89	96	102	95	81	108	83	62	87	87.5	11.7	13.4
d_5-pyridine	79	90	97	103	93	79	107	83	70	80	80.0	20.0	25.0
d_8-toluene	77	84	95	96	87	75	99	78	60	83	82.8	10.8	13.1
d_5-chlorobenzene	82	96	105	105	100	83	115	87	64	89	91.3	12.4	13.6
d_5-phenol	86	101	115	116	102	98	112	93	82	100	99.8	10.8	10.8
d_5-nitrobenzene	95	112	140	143	114	119	137	118	105	112	121	16.1	13.3
d_8-naphthalene	94	109	127	135	114	120	128	125	100	100	112	13.1	11.7
$^{13}C_6$-pentachlorophenol	39	135	142	137	46	90	127	203	83	104	129	50.1	38.9
Target compounds, ng/uL													
toluene	NF	NF	2.2	NF	NF	NF	2.0	2.6	NF	2.4			
Chlorobenzene	NF	20.0	37.6	21.1	2.8	16.6	26.4	33.0	15.0	30.8			
1,1,2,2-tetrachloroethane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF			
Other compounds, ng/uL													
4-methyl-2-pentanol	NF	61.8	180	35.2	2.4	127	150	124	129	136			
benzoic acid	31.0	106	73.6	93.8	42.0	86.2	92.6	89.2	60.9	61.9			
benzoyl chloride	37.6	23.2	15.4	22.2	22.2	16.1	20.8	18.6	13.3	13.0			
$C_{16}H_{33}CHO$	11.2	33.0	28.2	18.6	32.6	94.0	55.6	29.0	48.0	48.4			
diisooctyl phthalate	7.2	37.2	24.8	49.2	28.4	83.0	17.4	23.4	391	242			
Sample Volume (dscf)	0.0	35.1	61.0	35.6		60.2^c	32.0	60.5	32.2	58.4			

* Dynamic field spikes

# NF - not found.

** Two XAD-2 traps used during this run.

TABLE F-6. QUALITATIVE ANALYSIS

Part 1. Compounds Common to All Samples Characterized

Compound	Radian #8261 Run 1-A, XAD Scan # (Confidence Level)	Radian #8285 Blank, XAD	Radian #8267 Run 1-B, XAD	Radian #8339 Run 3-D, XAD	Radian #8327 Run 3-C, XAD
4-methyl-2-pentanol	344 (3)	326 (3)	330 (3)	324 (3)	338 (3)
ethyl carbamate	451 (2)	440 (2)	443 (2)	437 (2)	—
ethylbenzene	502 (3)	493 (3)	495 (3)	492 (3)	499 (3)
m-,*p*-xylene	513 (3)	504 (3)	507 (3)	504 (3)	510 (3)
o-xylene	547 (3)	539 (3)	542 (3)	539 (3)	544 (3)
benzaldehyde	635 (3)	630 (3)	633 (3)	631 (3)	634 (3)
hexanoic acid	643 (2)	639 (2)	641 (2)	640 (2)	645 (2)
phenol	653 (3)	649 (3)	651 (3)	649 (3)	652 (3)
dichlorobenzenes	694 (3), 702 (3), 730 (3)	—	692 (3), 728 (3)	698 (3), 727 (3)	700 (3), 728 (3)
acetophenone	763 (3)	760 (3)	762 (3)	761 (3)	762 (3)
benzoic acid	860 (3)	860 (3)	867 (3)	869 (3)	874 (3)
ethylbenzaldehydes	870 (3), 887 (3)	868 (3), 885 (3)	870 (3), 887 (3)	886 (3)	886 (3)
benzoyl chloride	983 (3)	982 (3)	984 (3)	983 (3)	983 (3)
ethylbenzoic acid	1038 (3), 1049 (3)	1039 (3), 1050 (3)	1041 (3), 1053 (3)	1040 (3), 1051 (3)	1040 (3), 1051 (3)
hexadecane	1251 (2)	—	1252 (3)	1251 (3)	1250 (3)
heptadecane	—	1327 (2)	1328 (3)	1327 (3)	1327 (3)
tetradecanoic acid	1368 (3)	1368 (3)	1369 (3)	—	—
phenanthrene	—	—	1424 (2)	1423 (3)	1422 (3)
diisooctyl phthalate	1984 (3)	1986 (3)	1987 (3)	1985 (3)	1984 (3)
$C_{16}H_{33}CHO$	1579 (2)	1578 (2)	1580 (2)	1583 (2)	1581 (2)

(continued)

TABLE F-6. (continued)

Part 2. Other Compounds Identified

Radian #0261
Run 1-A, XAD

o-chloroaniline (833, 3)
nonanoic acid (955, 2)
3-(1,1-dimethylethyl) phenol (990, 3)
$C_{13}H_{28}$ (994, 2)
tetradecane (1084, 2)
dodecanal (1095, 3)
$C_{12}H_{24}$ (1149, 3)
dodecanoic acid (1215, 2)
N-phenylaniline (1286, 3)
$C_{14}H_{28}$ (1311, 3)
2-(dodecyloxy) ethanol (1344, 1)
3-hexadecene (1458, 3)
hexadecanoic acid (1508, 2)

phthalate ester (1521, 3)
2-tetradecanol (1537, 2)
3-octadecene (1591, 3)
$C_{18}H_{36}$ (1664, 2)
2-heptadecanol (1713, 1)
phthalate ester (1975, 3)
phthalate ester (2277, 3)

$C_{20}H_{36}O$ (2473, 1)

Radian #0285
Blank, XAD

i-butyl acetate (419, 1)
methylstyrenes (675, 3; 679, 3)
heptanoic acid (752, 1)
methyl benzoate (792, 2)
nonanal (797, 2)
o-chloroaniline (831, 1)
dodecanal (904, 3)
nonanoic acid (954, 2)
dodecanoic acid (1214, 3)
N-phenylaniline (1281, 3)
pentadecanoic acid (1439, 2)
1-hexadecanol (1457, 3)
nonadecane (1469, 2)

9-hexadecenoic acid (1496, 3)
hexadecanoic acid (1508, 2)
phthalate ester (1521, 3)
5-octadecene (1591, 3)
$C_{16}H_{32}$ (1624, 3)
dihexyl hexanedioate (1634, 1)
4-(dimethylamino) benzoic
  acid (1728, 1)
2-tridecanol (1771, 1)
dioctyl hexanedioate (1815, 3)
triphenyl phosphate (1849, 3)
$C_{18}H_{38}O$, alcohol (1872, 1)
fatty acid methyl ester (1888, 1)
unknown (1919)
phthalate ester (2277, 3)
9-octadecenamide (2358, 1)
$C_{30}H_{50}$ (2473, 2)

Radian #0267
Run 1-B, XAD

chloropropene (373, 2)
alkoxy alkanol (423, 1)
5-methyl-2-hexanone (488, 1)
2-butoxyethanol (556, 1)
methylstyrenes (677, 3; 681, 3)
trimethylcyclohexanone (731, 1)
heptanoic acid (755, 1)
$C_{11}H_{24}$ (794, 2)
methyl 2,4-hexadienoate (797, 2)
methyl octanoate (819, 2)
o-chloroaniline (833, 3)
2,3-dichlorophenl (875, 3)
2-(2-ethoxyethoxy) ethanol
  acetate (880, 1)
naphthalene (899, 3)
3-phenyl-2-propenal (908, 2)
dichlorophenol (912, 3)
dimethylbenzaldehyde (935, 1)
dichloroaniline (952, 3)
nonanoic acid (957, 2)
1-(4-ethylphenyl) ethanone
  (970, 3; 990, 2)
$C_{13}H_{28}$ (995, 3)
methylnaphthalenes (1009, 3; 1027, 3)
decanoic acid (1048, 1)
trichlorophenol (1058, 2)
tetradecane (1086, 3)
tetrachlorobenzene (1089, 1)
trichlorophenol (1089, 1)
pentadecane (1171, 2)
methyl methylundecanoate (1191, 2)
(1-butylhexyl)benzene (1209, 3)
(1-propylheptyl)benzene (1216, 2)
(1-ethyloctyl)benzene (1233, 3)
(1-methylnonyl)benzene (1262, 3)
N-phenylaniline (1287, 3)
(1-propyloctyl)benzene (1295, 3)
$C_{19}H_{40}$ (1334, 2)
(1-methyldecyl)benzene (1340, 3)
methyl tetradecanoate (1347, 3)
(1-pentylheptyl)benzene (1357, 3)
(1-butyloctyl)benzene (1361, 3)
(1-ethyldecyl)benzene (1388, 3)
$C_{15}H_{32}$ (1409, 3)
(1-methylundecyl)benzene (1415, 3)
(1-butylnonyl)benzene (1433, 1)
(1-propyldecyl)benzene (1442, 1)
1-phenyl-1,2-propanedione (1467, 2)
nonadecane (1471, 2)
dibutyl propanedioate (1487, 1)
methyl methylundecanoate (1489, 1)
5-octadecene (1497, 2)
hexadecanoic acid (1509, 2)
butyl octyl phthalate (1522, 2)
eicosane (1536, 1)
i-propyl hexadecanoate (1552, 3)
$C_{16}H_{30}$ (1580, 3)
$C_{20}H_{40}$ (1593, 2)
$C_{13}H_{28}$ (1600, 1)
octadecanoic acid (1636, 2)
dioctyl hexanedioate (1816, 3)
dihexyl nonanedioate (1873, 1)
$C_{16}H_{25}N$ (2474, 1)

(continued)

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TABLE F-6. (continued)

Part 2. Other Compounds Identified (continued)

Radian #8339
Run 3-D, XAD

dibromomethane (246, 3)
1,4-dioxane (257, 3)
4,4-dimethyl-2-pentanone (375, 1)
1-chloro-1-propene (380, 3)
dibromochloromethane (396, 3)
hexanal (404, 2)
butyl acetate (428, 1)
Cl_2 compound (441, 1)
furfural (454, 1)
3,3-dimethyl-2-hexanone (460, 1)
bromoform (532, 3)
2-heptanone (537, 2)
heptanal (553, 2)
$C_3H_3Br_2F$ (tentative) (565)
bromobenzene (597, 3)
methylbenzaldehyde (677, 2)
methylstyrene (677, 3)
octanal (683, 3)
Br_2 compound (695)
C_8H_{14} (705, 1)
2-methyl-1-butanol acetate (756, 2)
alkoxy alkanol (771)
unknown (785)
unsaturated C_4-alkylbenzene (793, 2)
brominated compound (832)
naphthalene (898, 3)
Br_2 compound (919)
nonanoic acid (956, 3)
ethylacetophenone (969, 3)
$C_{13}H_{28}$ (993, 3)
methylnaphthalenes (1008, 3; 1026, 2)
1-(1,1-dimethylethyl)-4-ethoxybenzene (1075, 3)
Br compound (1140)
$C_{15}H_{32}$ (1169, 3)
Br_3 compound (1222)
$ClBr_2$ compound (1228)
$ClBr_2$ compound (1282)
tribromophenol (1308, 3)
Br compound (1323)
Br_2 compound (1345)
tribromoaniline (1362, 3)
hexadecanoic acid (1507, 3)
phthalates (1520, 2140, 2276)
2,3-dibromothieno[3,2-C] pyridine (1548, 2)
nonadecane (1810, 3)
$C_{21}H_{44}$ (1910, 1)
$C_{21}H_{44}$ (2031, 1)

Radian #8327
Run 3-C, XAD

dibromomethane (230, 3)
1,4-dioxane (241, 3)
chloropropene (368, 2)
furfural (445, 1)
bromoform (526, 3)
3-bromo-1-propyne (560, 2)
bromobenzene (593, 3)
C_3-alkylbenzene, methylstyrene (675)
alkoxy alkanol (771)
Br_2compound (919)
nonanoic acid (956, 2)
ethylacetophenone (970, 3)
C_2-alkylacetophenone (990, 2)
$C_{13}H_{28}$ (994, 3)
methylnaphthalenes (1009, 2; 1026, 2)
bromodichlorophenol (1142, 2)
$C_{15}H_{32}$ (1170, 2)
C_3-alkylnaphthalene (1195, 3)
Cl_2Br compound (1195)
dodecanoic acid (1215, 2)
Cl_3Br compound (1223)
Cl_3Br compound (1228)
Cl_3Br compound (1282)
Cl_3Br compound (1309)
tribromophenol (1309, 3)
$C_{19}H_{40}$ (1332, 3)
Br_2 compound (1345)
tribromoaniline (1362, 2)
hexadecanoic acid (1508, 2)
phthalates (1521, 2277)
Cl_2Br compound (1536)

were common to all the XAD-2® extracts characterized are listed together. The identification of 4-methyl-2-pentanol was confirmed by injection of an authentic standard. This compound has frequently been observed in XAD-2® extracts and may be an artifact of this process. Another compound of interest observed in most of the extracts analyzed in this study is listed in Table F-6 as $C_{16}H_{33}CHO$. This compound is a major constituent of all of the chromatograms and is not definitively identified by computerized library search. A mass spectrum of this compound is shown in Figure F-1. An inspection of the spectrum shows peaks characteristic of the fragmentation pattern exhibited by aliphatic aldehydes. A molecular ion at mass 254 suggests that the compound is an aliphatic (as opposed to cyclic or unsaturated) aldehyde, with a peak at m/z 210 being characteristic of a mass spectrometric rearrangement process which occurs in this type of compound and indicates the presence of hydrogen in the position gamma to the carbonyl carbon. A further interesting note on the presence of this compound is its occurrence in all of the media studied, not just XAD-2® extracts. This observation suggests that the compound may be present for reasons other than XAD-2® artifact formation.

The two samples from Run 3 showed extensive presence of brominated compounds. The presence of dibromomethane was anticipated, since this compound was spiked into the waste during Run 3. However, bromoform, bromobenzene, dibromochloromethane, tribromophenol, tribromoaniline, and other compounds with both chlorine and bromine, which could not be identified, were also observed in one or both of the samples. Hexachlorocyclopentadiene was spiked during Runs 4 and 5, but no extensive characterization of compounds was performed for these samples. Based on the observations of Run 3 samples (dibromomethane feed), substantial numbers of variously chlorinated compounds would be expected if series 4 and 5 samples were characterized.

Extracted ion current profiles have been plotted for various samples, using ions characteristic of different compound series. Figure F-2 shows the extracted ion current profile obtained for mass 57, characteristic of saturated hydrocarbons, in Sample 8376, an extract of XAD-2® from Run 5-B. Figure F-3 shows the extracted ion current profile of mass 91, characteristic of aromatic systems, for the same sample.

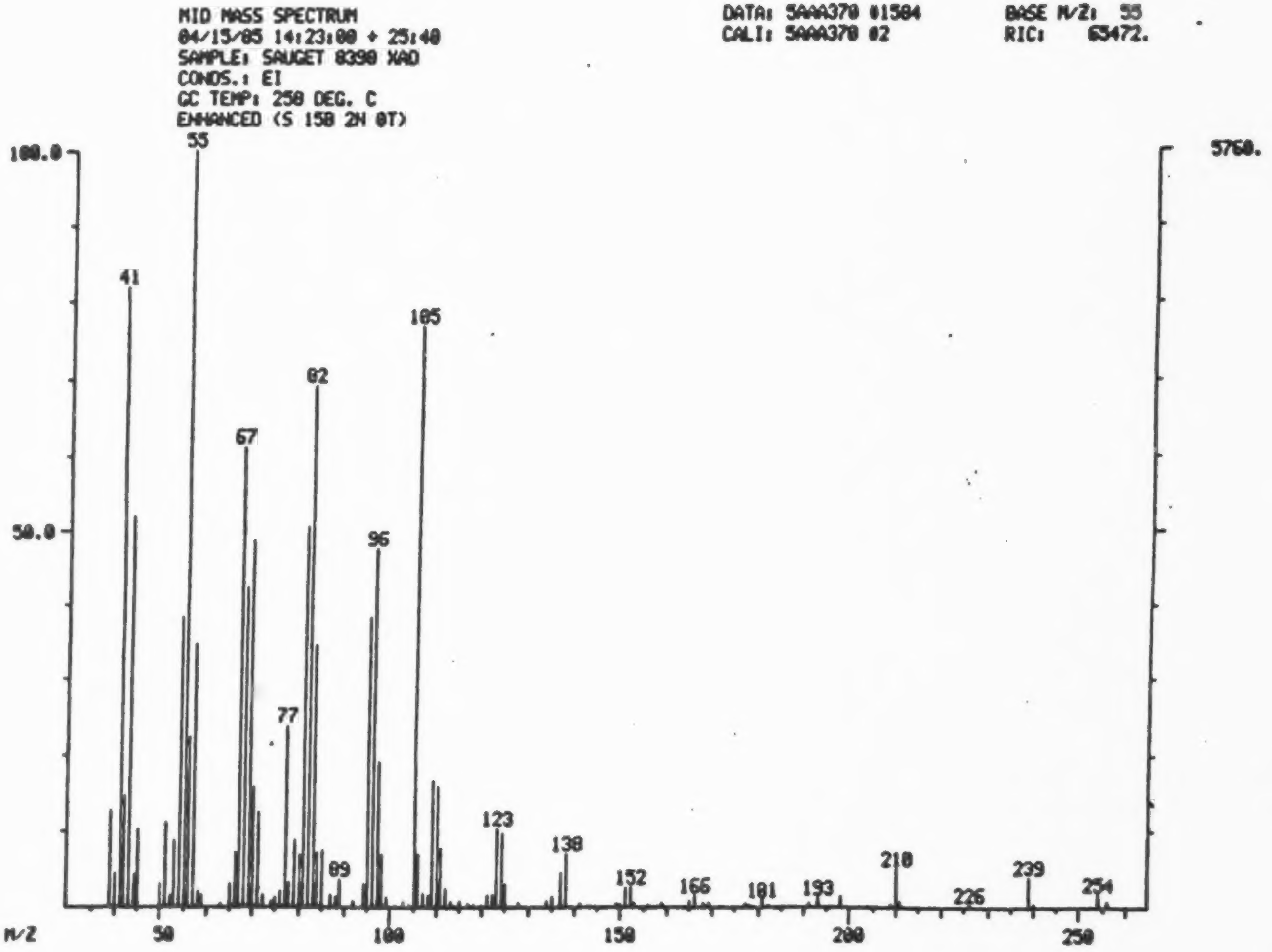

Figure F-1. Mass spectrum of the compound identified as $C_{16}H_{33}CHO$, present in all extracts.

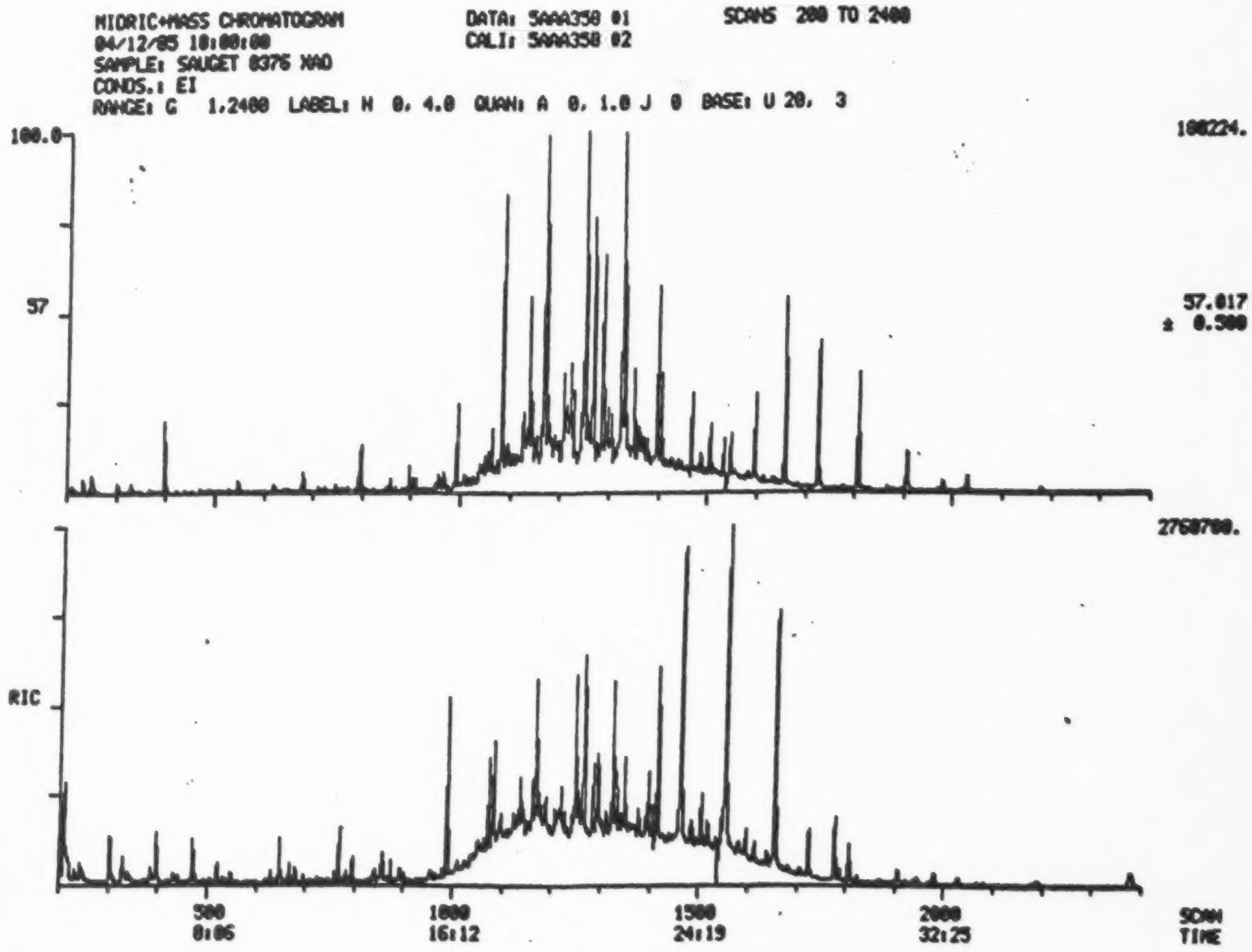

Figure F-2. Extracted ion current profile of mass 57, characteristic of saturated hydrocarbons, for Sample 8376, an extract of XAD-2® from Run 5-B.

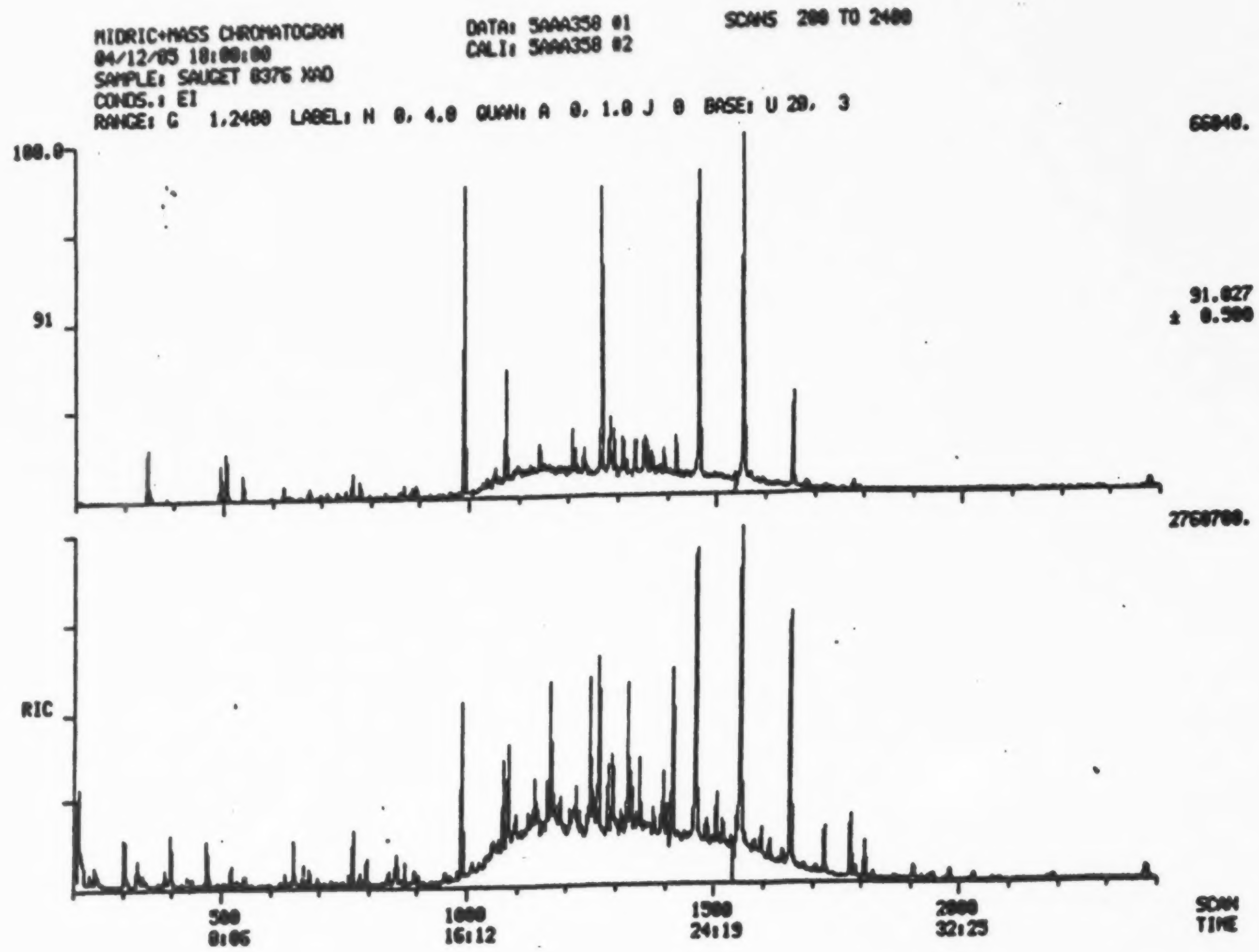

Figure F-3. Extracted ion current profile of mass 91, characteristic of aromatic systems, for Sample 8376, XAD-2® extract, Run 5-B.

Figure F-4 shows extracted ion current profiles of masses 74 and 87, characteristic of methyl esters of aliphatic carboxylic acids for the same sample. Figure F-5 shows extracted ion current profiles of masses 60 and 73, characteristic of aliphatic carboxylic acids, for the XAD-2® extract of Sample 8267, from Run 1-B. Figure F-6 shows the extracted ion current profile of mass 149, characteristic of phthalate esters, for the XAD-2® extract of Sample 8267, from Run 1-B. These figures show that saturated hydrocarbons are extensively present, with the regular n-alkane series ranging from approximately C_{14}-C_{18}. Earlier-eluting hydrocarbons have many branched species interspersed with the n-alkanes. Aromatic systems, starting with toluene and continuing (for some samples) through C_5-C_{12} alkylbenzenes, are also observed in the samples. There are a few methyl esters, but for the most part, this is not a class of compounds which is present either in large numbers or in large amounts. Some of the samples show the presence of carboxylic acids, which have been cited in the literature as possible artifacts of XAD-2® extraction with polar solvents. In the present situation, no polar solvents such as diethyl ether were used to extract the XAD-2®; extraction was performed with methylene chloride. Also, no non-XAD-2® extracts were characterized to determine if the carboxylic acids were also present when no XAD-2® is extracted. The phthalate esters are plasticizers, and are virtually ubiquitous as contaminants. These peaks may be observed as a result of use of, and subsequent concentration of, organic solvent or as the result of contact of any part of the sample system or solvent with plastic containers or tubing. Presence of phthalates as a function of the use and concentration of methylene chloride is very highly probable, since these phthalate esters are observed both in XAD-2® extracts and in all other samples studied as well.

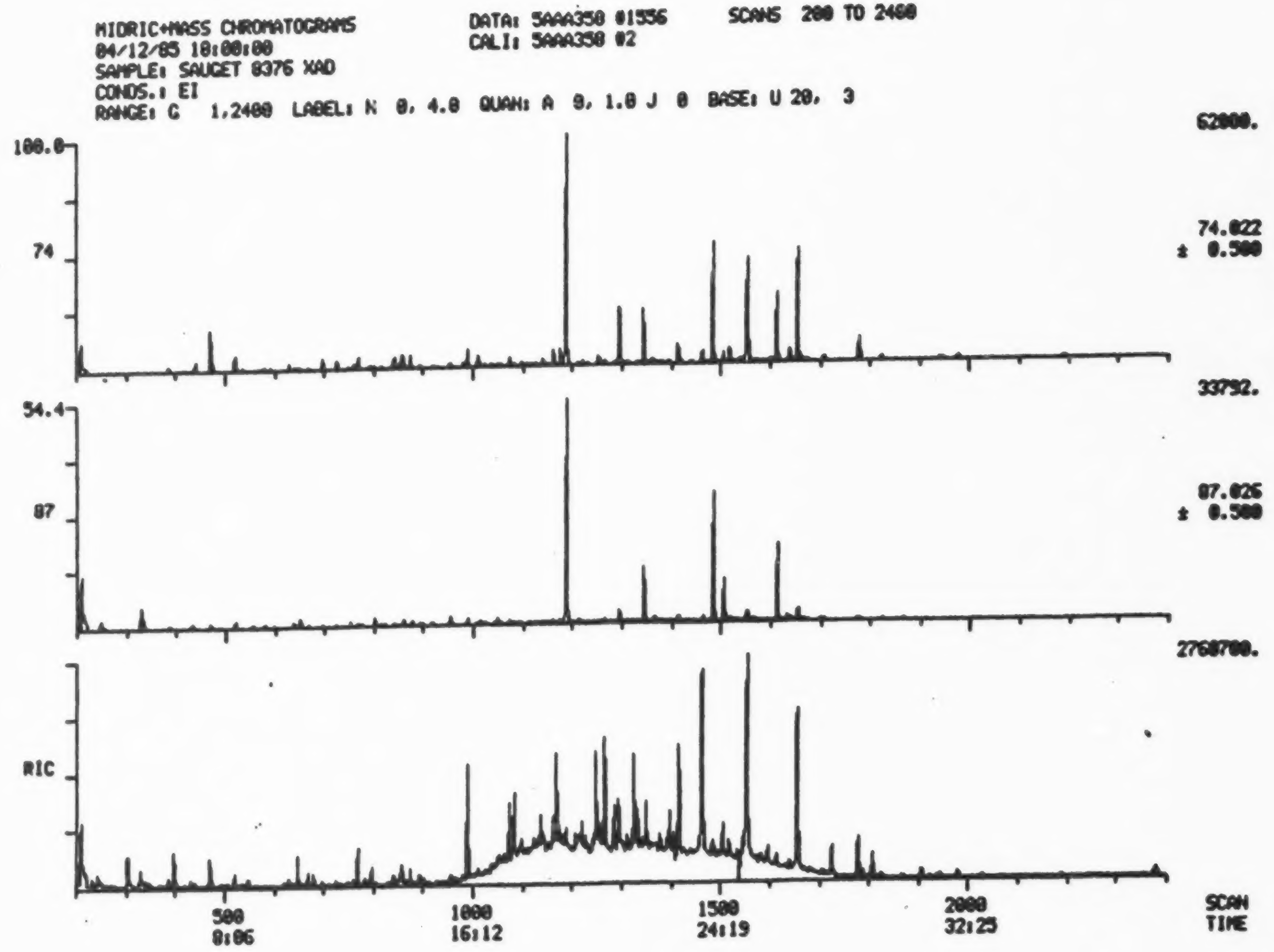

Figure F-4. Extracted ion current profile of mass 149, characteristic of phthalate esters (plasticizers) for the XAD-2® extract of Sample 8267, Run 1-B.

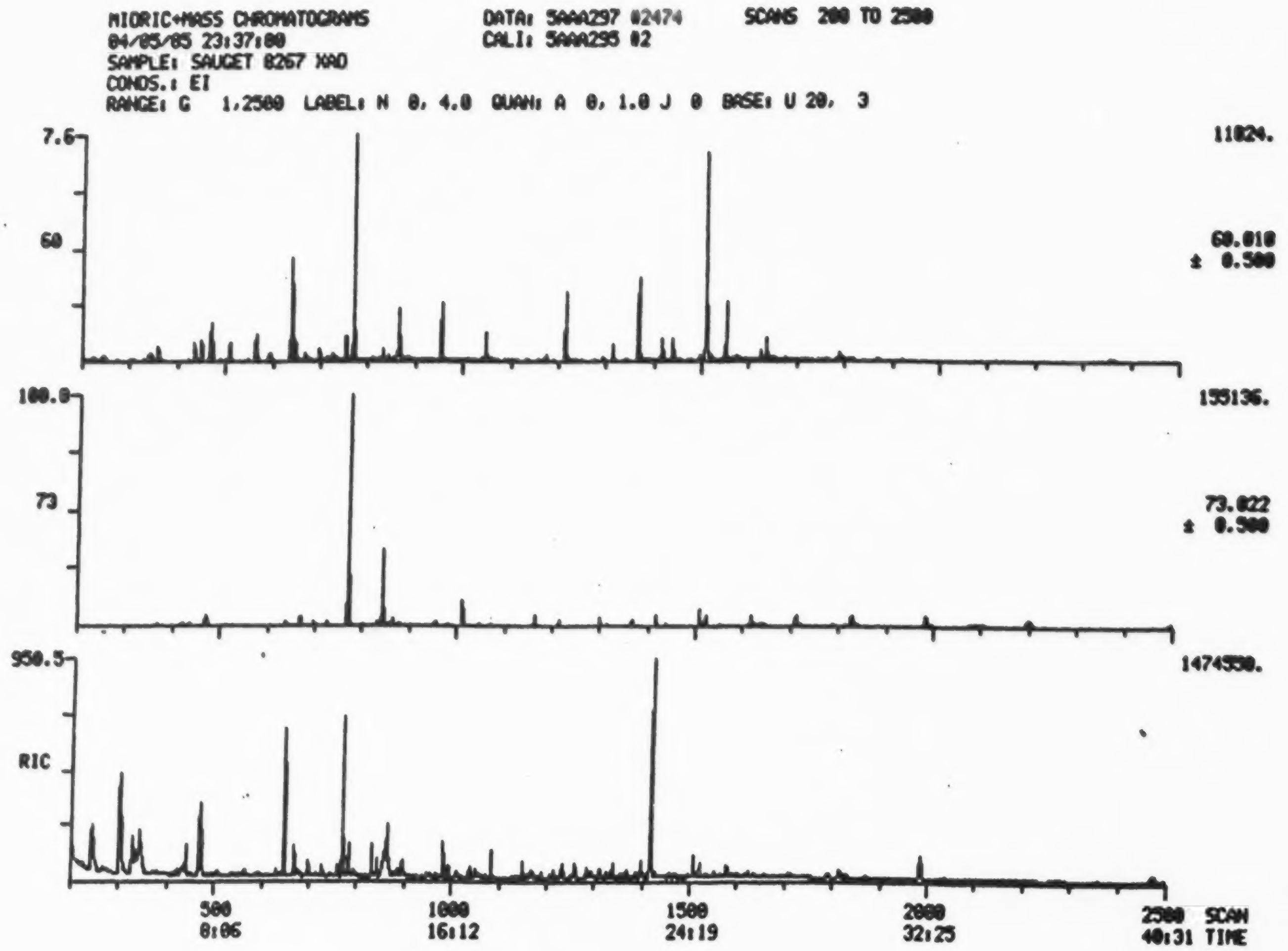

Figure F-5. Extracted ion current profile of masses 74 and 87, characteristic of methyl esters of aliphatic carboxylic acids, for the XAD-2® extract of Sample 8376, Run 5-B.

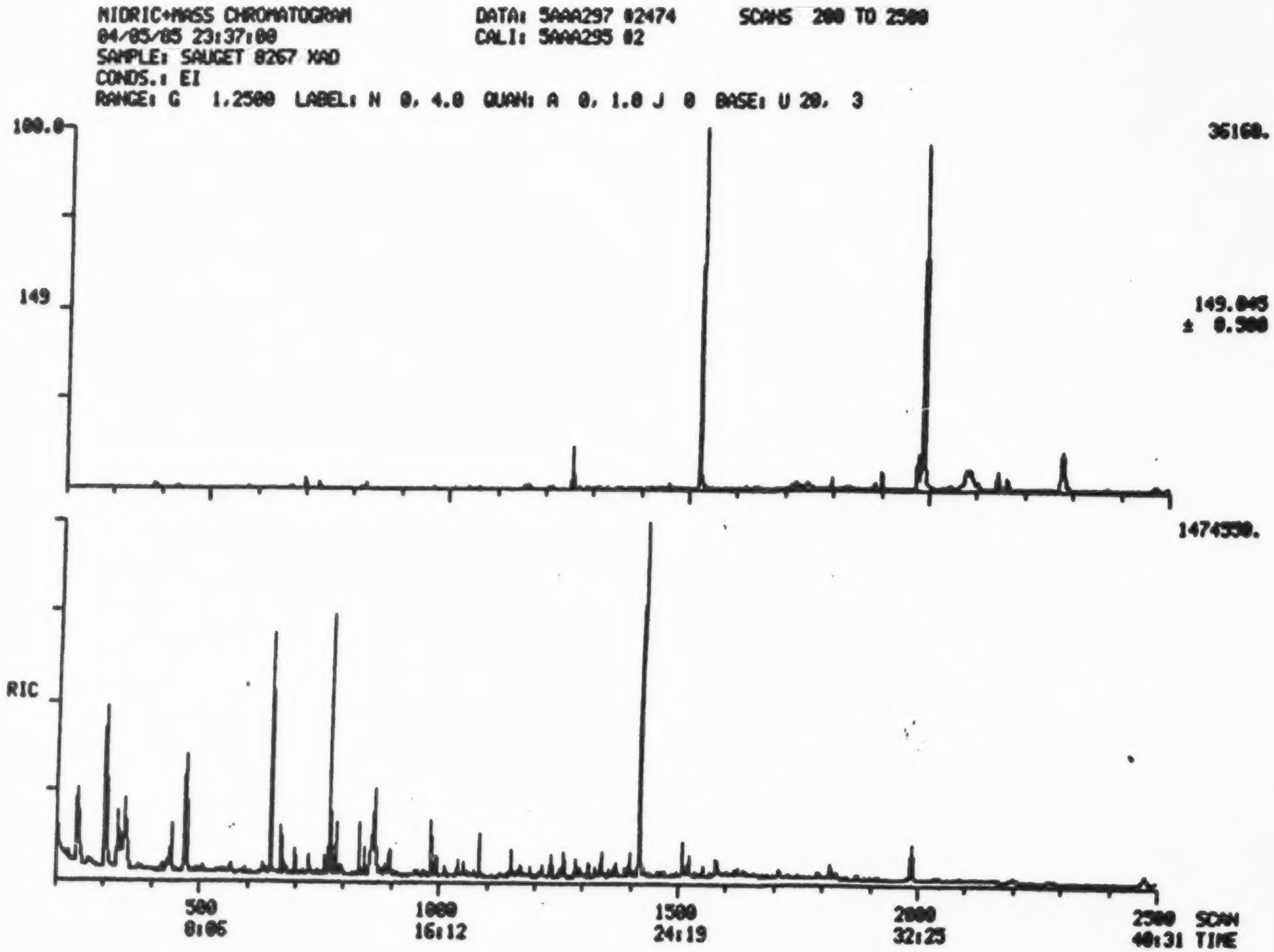

Figure F-6. Extracted ion current profile of masses 60 and 73, characteristic of aliphatic carboxylic acids, for the XAD-2® extract of Sample 8267, Run 1-B.

APPENDIX G

QUALITY ASSURANCE/QUALITY CONTROL

The quality assurance (QA) activities used for the field test evaluation of the Semi-VOST sampling and analysis methodology are detailed in the Quality Assurance Project Plan for that field test.(1) The QA project plan was designed according to the guidelines proposed in the EPA draft document "Guidelines and Specifications for Preparing Quality Assurance Project Plans," QAMS-005/80.

In this appendix, the following quality control/quality assurance (QA/QC) data are presented: (1) a summary of field quality control procedures; and (2) data from the analyses of check samples prepared by the Research Triangle Institute. Representative examples are presented for: (1) control charts for the daily analyses of calibration standards to monitor stability of response factors used to calculate recoveries of surrogates and quantities of compounds; (2) daily tuning data from the gas chromatograph/mass spectrometer/data system for decafluorotriphenylphosphine, the compound used as a tuning standard; and (3) data from the column performance standard, analyzed weekly to monitor possible deterioration of the chromatographic column.

QUALITY CONTROL OF FIELD ACTIVITIES

Calibrations of Field Equipment

The consoles, thermocouples, temperature gauges, and probe nozzles were calibrated as described in Section 3.4.2 of EPA document 600/4-77-027b, Quality Assurance Handbook for Air Pollution Measurement Systems. The type S pitot tube assembly was calibrated using the procedure in Section 3.1.2 of EPA Reference Method 2.

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(1) Quality Assurance Project Plan: Field Test Evaluation of the Semi-VOST Sampling and Analysis Methodology at the Trade Waste Incineration Facility; Sauget, Illinois; Radian Corporation, December 10, 1984.

The spiking system was designed by Radian Corporation and was calibrated by following the procedure outlined in the QA/QC plan. In addition to the calibration and check out of the dynamic spiking system in the laboratory prior to the field test, the procedures for checking the system output both for concentration of the VOC and flow from the mass flow controllers as depicted in Figure 2 of the experiment were carried out in the field just prior to testing and immediately following testing.

Quality Objectives

In order to ensure the completeness of the field data, several quality objectives were put in place. They included leak checks, consistency of clean-up procedures, monitoring the flow, temperature and vacuum gauges throughout the testing period, noting abnormalities during testing, and complete documentation of data.

One of the criteria for sampling for each run was the need to obtain good (<.02 CFM) leak checks on each of the four trains that were to be run simultaneously. In all cases, this leak check was satisfactory both before and after testing. In one case (Run 3), the filters plugged on the two trains which were conducting the 4-hour run. Satisfactory leak checks were performed before disassembly of the plugged trains and prior to conducting tesing with the new filters.

To ensure consistency between the trains, one person was assigned to clean up, recover, and re-assemble the glassware. This protocol served to eliminate the propogation of multiple operator variance for the method precision experiments.

The isokinicity was not within the 90 to 110 percent range for all runs. Wherever possible, this criterion was followed. However, in some runs, maintaining the flow rate of 0.5 CFM through the train was required for the experiment. Since the flow through the stack was variable, only one of these requirements could be met at times.

Other Effects on Sampling Quality

During testing, two factors occurred that were not anticipated from the pre-test visits. The first of these factors was the extremely cold weather conditions that prevailed during the testing period. An attempt to test at the facility had been made 2 weeks earlier and had been aborted because of low temperatures and high wind conditions (wind chill factors of -77°F). At that time, it was determined that the sampling locations should be enclosed with a wind protective shell. Plant personnel enclosed the test scaffolding with PVC film tacked on a wooden frame. During testing, temperatures inside the test location ranged from 30 to 50°F while the outside temperatures ranged from 0 to 25°F with wind chills as low as -22°F. With this precaution taken, the impinger trains and dynamic spiking system were rarely subjected to freezing temperatures during sampling. While these temperatures may have had an effect on the sampling system, it would not be an abnormal effect for winter sampling.

The second factor which became evident during the testing period was the variability of the process feed. During the testing periods, solid waste of variable contents were fed to the incinerator every 5 to 10 minutes. This caused a minor upset period during the time of the feed. There should be no effect on the precision of measurements within a quad run conducted over the same time period but there could be effects between runs conducted over differing time periods.

ANALYSIS OF CHECK SAMPLES SUPPLIED BY THE RESEARCH TRIANGLE INSTITUTE

The Research Triangle Institute prepared two check samples for analysis by the Radian Research Triangle Park Laboratories. These samples consisted of two XAD-2® modules which had been spiked with known quantities of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane. Four blanks were also supplied with these check samples. Two of the blanks were reserved in the laboratory and two were sent to the field as "trip blanks." The results of the analyses are shown in Table G-1. The spiked compounds were not observed in the blank samples. With the exception of pentachlorophenol, surrogate recoveries were consistent and reasonably near 100 percent.

Table G-2 shows the comparison of the observed values with the "expected" levels of the three compounds spiked onto the XAD-2® by the Research Triangle Institute. The precision of the spiking methodology employed by RTI is estimated as 20.6, 33.8, and 10.5 percent relative for toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane, respectively. Recoveries of approximately 80 percent were obtained for the deuterated surrogates which Radian added to samples M-1 and P-1. These values are reasonable for both toluene and chlorobenzene following extraction and K-D concentration. The surrogate-corrected recovery efficiency for toluene was 87 and 89 percent for samples M-1 and P-1, respectively. Corresponding recoveries for chlorobenzene were 88 and 90 percent. All values were within the estimated acceptance ranges for RTI's expected loadings. Therefore, no bias was introduced during the analyses of the RTI spiked samples in the Radian Laboratory.

DAILY CALIBRATION OF THE GC/MS SYSTEM

An initial calibration of the GC/MS system was performed using triplicate injections at each of five concentration levels to generate a response factor data base. The generation of this data base is discussed in Appendix F. A comparison of the 15-point data base with a 5-point data base (one injection at each of the five concentration levels) is also discussed in Appendix F. The protocol for the analysis of field samples required the analysis of two calibration standards each day, one at the beginning of the day and one at the end of the day. Two presentations of the results of these daily analyses are made - control charts for the individual compounds and a tabular summary of the values. Figures G-1 through G-23 are the control charts. The mean response factor from the 15-point data base is shown as the mean value in the control charts. Around that mean, the standard deviation of the values in the data base is shown as 1 σ, 2 σ, and 3 σ. Nearly all of the points obtained in the daily analyses of calibration samples are within the 3 σ range of the control charts. Table G-3 presents the same information in tabular form. The value of the response factor calculated for each ion of each compound is shown with the date for the analysis. The mean of this set of daily values is calculated, as is the standard deviation and the percent coefficient of variation. The mean of the set of daily values is then compared to the mean of the same response factor from the 15-point data base, and a relative percent difference is calculated. The values differ by 15 percent or less, showing excellent stability for the analytical instrument and entirely acceptable reproducibility of values for the response factors over the entire period of the analytical determinations.

DAILY TUNING DATA FOR THE GC/MS SYSTEM

The compound decafluorotriphenylphosphine (DFTPP) was used as the daily tuning standard for the mass spectrometer. The criteria for acceptability of the tune of the mass spectrometer are shown in Table 4-2 of Appendix A. No analysis was performed until the instrument had satisfied tuning criteria every day. The data obtained for the daily analyses of DFTPP are shown in three forms. The first entry for every day is a chart showing the ions specified in the table of criteria, with a comparison of the values obtained with the specified values. The second set of information shows a plotted mass spectrum obtained daily from the analysis of DFTPP, and the third set of data includes a list of the masses and intensities obtained for this compound. An inspection of the values obtained for analysis of DFTPP also illustrates the excellent stability of the mass spectrometer during this study.

ANALYSIS OF THE COLUMN PERFORMANCE SOLUTION

The column performance solution consists of a mixture of compounds which are intended to test the condition of the chromatographic column in order to decide whether column maintenance should be performed on a given chromatographic column. Critical parameters are resolution, separation number, and peak asymmetry. The calculations and values obtained are described below.

Column Performance Data

Components of the column performance standard:

- octanone
- decane
- 1-octanol
- undecane
- 2,6-dimethylphenol
- 2,6-dimethylaniline

- naphthalene
- dodecane
- tridecane

Resolution (octanone, decane):

$$R = \frac{2\ (\text{distance between peak tops})}{(\text{width of peak 1 + width of peak 2})} \quad \text{at base}$$

Separation number (undecane, tridecane)

$$SN = \frac{(\text{distance between peak tops})}{(\text{width of peak 1 + width of peak 2})} \quad \text{at half-height}$$

Percent peak asymmetry factor (2,6-dimethylphenol (2,6-DMP), 2,6-methylaniline (2,6-DMA), 1-octanol)

$$\text{Percent PAF} = \frac{(\text{width of back half of peak})}{(\text{width of front half of peak})} \times 100 \text{ at 10\% height}$$

Values calculated:

	4/01/84	4/09/85	4/15/85
R	1.7	2.0	2.1
SN	35	41	47
Percent PAF			
2,6-DMP	50	91	100
2,6-DMA	67	71	70
1-octanol	64	73	85

TABLE G-1. ANALYSIS RESULTS OF RTI XAD-2® SAMPLES

Compounds	Lab blank 1	Lab blank XAD	Travel blank XAD	Travel blank XAD	Spike P-1	Spike M-1	Mean	SD	% CV
Surrogate Compounds % Recoveries									
d_8-1,4-dioxane	75	79	80	103	82	83	83.7	9.9	11.8
d_5-pyridine	84	83	78	105	85	88	87.2	9.3	10.7
d_8-toluene	75	71	75	92	79	79	78.5	7.3	9.2
d_5-chlorobenzene	75	78	84	111	85	86	86.5	12.8	14.7
d_5-phenol	92	83	95	115	100	103	98.0	10.8	11.1
d_5-nitrobenzene	91	91	103	137	111	120	108.8	17.8	16.4
d_8-naphthalene	91	85	111	121	105	104	102.8	13.1	12.8
$^{13}C_6$-pentachlorophenol	45	113	10	150	69	37	70.7	52.1	73.7
Target Compounds, ng/vL									
Toluene	NF*	0.05	0.4	1.0	24.2	24.0			
Chlorobenzene	NF	NF	NF	NF	25.2	25.2			
1,1,2,2-tetrachloroethane	NF	NF	NF	NF	24.8	24.6			
Other Compounds ng/vL									
4-methyl-2-pentanol	6.1	59.6	5.2	19.2	5.0	5.2			
Benzoic acid	23.7	45.8	44.4	77.4	49.2	45.6			
Benzoyl chloride	58.3	17.0	57.6	51.6	39.4	55.2			
$C_{16}H_{33}CHO$	16.3	94.8	286.6	42.6	271.2	191.4			
Diisooctyl phthalate	88.6	55.6	67.6	184.2	30.4	26.8			

* NF = not found.

TABLE G-2. COMPARISON OF ANALYTICAL RESULTS FOR XAD-2® SPIKED BY RTI

Sample	Compound	Expected loading* (µg)	Measured loading (µg)	Recovery efficiency (percent)	Corrected loading† (µg)	Corrected recovery efficiency (percent)
M-1	Toluene	175±36.1	120	69	152	87
	Chlorobenzene	168±56.8	126	75	147	88
	1,1,2,2-tetrachloroethane	162±17.0	123	76	-§	-§
P-1	Toluene	172±35.4	121	70	153	89
	Chlorobenzene	165±55.8	126	76	148	90
	1,1,2,2-tetrachloroethane	159±16.7	124	78	-§	-§

* Expected RTI loading ± uncertainty (µg) introduced by loading precision.

† Measured loading as corrected by the recovery efficiency of the deuterated internal standard.

§ No deuterated internal standard available.

TABLE G-3. DAILY CALIBRATION SAMPLES

Compound	Ion	4/8	4/9	4/9	4/10	4/10	4/11	4/11	4/12	4/13	4/15
d_{10}-phenanthrene	160	113889	123365	124011	135753	143404	131496	163875	132353	138661	141258
d_8-1,4-dioxane	62	0.488	0.474	0.484	0.494	0.442	0.485	0.334	0.498	0.431	0.498
	96	1.368	1.441	1.361	1.443	1.277	1.429	1.070	1.487	1.342	1.526
d_5-pyridine	52	1.441	1.383	1.358	1.239	1.160	1.250	1.172	1.287	1.194	1.147
d_8-toluene	54	0.952	0.994	0.956	0.964	0.841	0.974	0.887	1.019	0.867	0.934
	70	1.077	1.120	1.110	1.075	0.947	1.062	1.035	1.141	1.041	1.104
d_5-chlorobenzene	54	1.965	1.985	1.983	2.024	1.805	1.987	1.845	2.123	1.902	1.941
	117	4.509	4.661	4.588	4.601	4.110	4,494	5.094	4.861	4.591	4.792
	119	1.468	1.502	1.466	1.480	1.332	1.448	1.638	1.580	1.459	1.534
d_5-phenol	71	1.897	1.719	1.883	1.731	1.560	1.580	1.527	1.729	1.691	1.457
d_5-nitrobenzene	98	0.432	0.369	0.433	0.302	0.334	0.314	0.400	0.337	0.356	0.306
	128	1.151	0.958	1.188	0.871	0.877	0.778	1.175	0.847	0.985	0.856
d_8-naphthalene	108	1.181	1.163	1.175	1.174	1.066	1.112	1.179	1.206	1.164	1.152
$^{13}C_6$-pentachlorophenol	270	0.264	0.231	0.372	0.259	0.304	0.275	0.449	0.292	0.316	0.255
	272	0.443	0.399	0.589	0.436	0.480	0.455	0.687	0.471	0.506	0.437
toluene	51	0.911	0.997	0.917	0.873	0.894	0.892	0.832	0.881	0.833	0.848
	65	1.309	1.333	1.356	1.396	1.237	1.368	1.343	1.397	1.279	1.382
	91	7.187	7.454	7.430	7.404	6.551	7.201	7.725	7.634	6.969	7.425
chlorobenzene	51	1.877	1.962	1.846	2.040	1.678	1.999	1.798	2.035	1.726	1.834
	112	4.432	4.623	4.480	4.392	3.965	4.327	4.906	4.680	4.410	4.559
	114	1.389	1.437	1.407	1.389	1.256	1.353	1.556	1.488	1.391	1.422
1,1,2,2-tetrachloroethane	83	4.404	4.618	4.447	4.603	3.987	4.458	4.572	4.752	4.429	4.437
	131	0.322	0.323	0.325	0.342	0.290	0.310	0.362	0.351	0.338	0.332
	168	0.207	0.200	0.203	0.191	0.176	0.195	0.278	0.219	0.208	0.225

(continued)

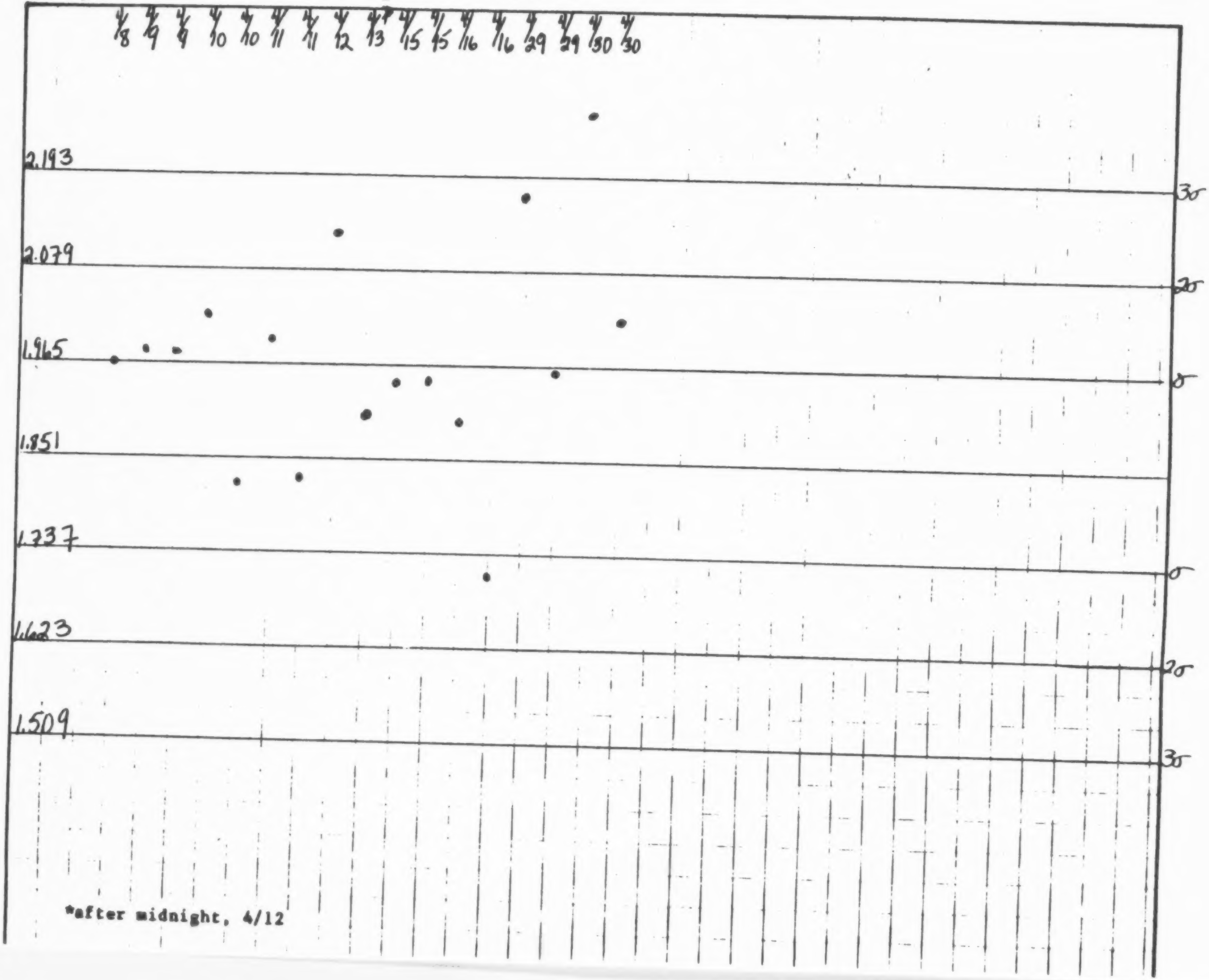
TABLE G-3. (continued)

Compound	Ion	4/15	4/16	4/16	4/29	4/29	4/30	4/30	Mean	SD	%CV	Database Mean	RPD
d_{10}-phenanthrene	160	150393	146728	127148	98063	74703	76713	74490	123312	27216	22.1		
d_8-1,4-dioxane	62	0.491	0.521	0.418	0.542	0.465	0.524	0.460	0.475	0.049	10.4	0.472	0.6
	96	1.484	1.780	1.411	1.490	1.168	1.322	1.233	1.390	0.159	11.4	1.359	2.3
d_5-pyridine	52	1.220	1.106	1.031	1.439	1.365	1.391	1.366	1.268	0.123	9.7	1.426	11.1
d_8-toluene	54	0.916	0.930	0.843	1.011	0.892	1.048	0.968	0.941	0.061	6.5	0.899	4.7
	70	1.045	1.150	0.982	1.139	0.977	1.117	1.013	1.067	0.062	5.8	1.025	4.1
d_5-chlorobenzene	54	1.944	1.894	1.712	2.181	1.959	2.277	2.015	1.973	0.134	6.8	1.851	6.6
	117	4.934	5.361	4.582	4.523	3.847	4.198	3.998	4.573	0.386	8.4	4.345	5.2
	119	1.604	1.723	1.468	1.463	1.229	1.353	1.277	1.472	0.127	8.6	1.374	7.1
d_5-phenol	71	1.601	1.409	1.469	1.655	1.533	1.646	1.628	1.630	0.137	8.4	1.819	10.4
d_5-nitrobenzene	98	0.356	0.315	0.359	0.420	0.403	0.390	0.419	0.367	0.045	12.3	0.409	10.3
	128	1.082	1.094	1.030	1.081	0.936	0.860	1.017	0.987	0.128	12.9	1.102	10.4
d_8-naphthalene	108	1.202	1.041	1.066	1.222	1.154	1.199	1.126	1.152	0.053	4.6	1.124	2.5
$^{13}C_6$-pentachlorophenol	270	0.345	0.381	0.431	0.280	0.291	0.261	0.281	0.311	0.063	20.4	0.311	0
	272	0.583	0.639	0.694	0.473	0.474	0.418	0.463	0.509	0.093	18.4	0.499	2.0
toluene	51	0.838	0.894	0.883	0.942	0.827	0.960	0.809	0.884	0.051	5.8	0.858	3.0
	65	1.322	1.462	1.204	1.445	1.250	1.450	1.261	1.341	0.077	5.8	1.279	4.8
	91	7.468	8.236	7.060	7.483	6.193	6.948	6.401	7.221	0.506	7.0	7.012	3.0
chlorobenzene	51	1.718	1.773	1.577	1.994	1.803	2.081	1.806	1.856	0.143	7.7	1.771	4.8
	112	4.743	5.119	4.388	4.431	3.701	4.051	3.847	4.415	0.367	8.3	4.229	4.4
	114	1.477	1.620	1.378	1.412	1.194	1.315	1.221	1.394	0.110	7.9	1.329	4.9
1,1,2,2-tetrachloroethane	83	4.707	4.720	4.172	4.248	3.616	4.229	3.709	4.359	0.334	7.7	4.247	2.6
	131	0.362	0.363	0.315	0.322	0.282	0.298	0.296	0.325	0.025	7.8	0.310	4.8
	168	0.236	0.275	0.213	0.200	0.173	0.180	0.179	0.209	0.031	14.8	0.199	5.0

RESPONSE FACTOR CONTROL CHARTS

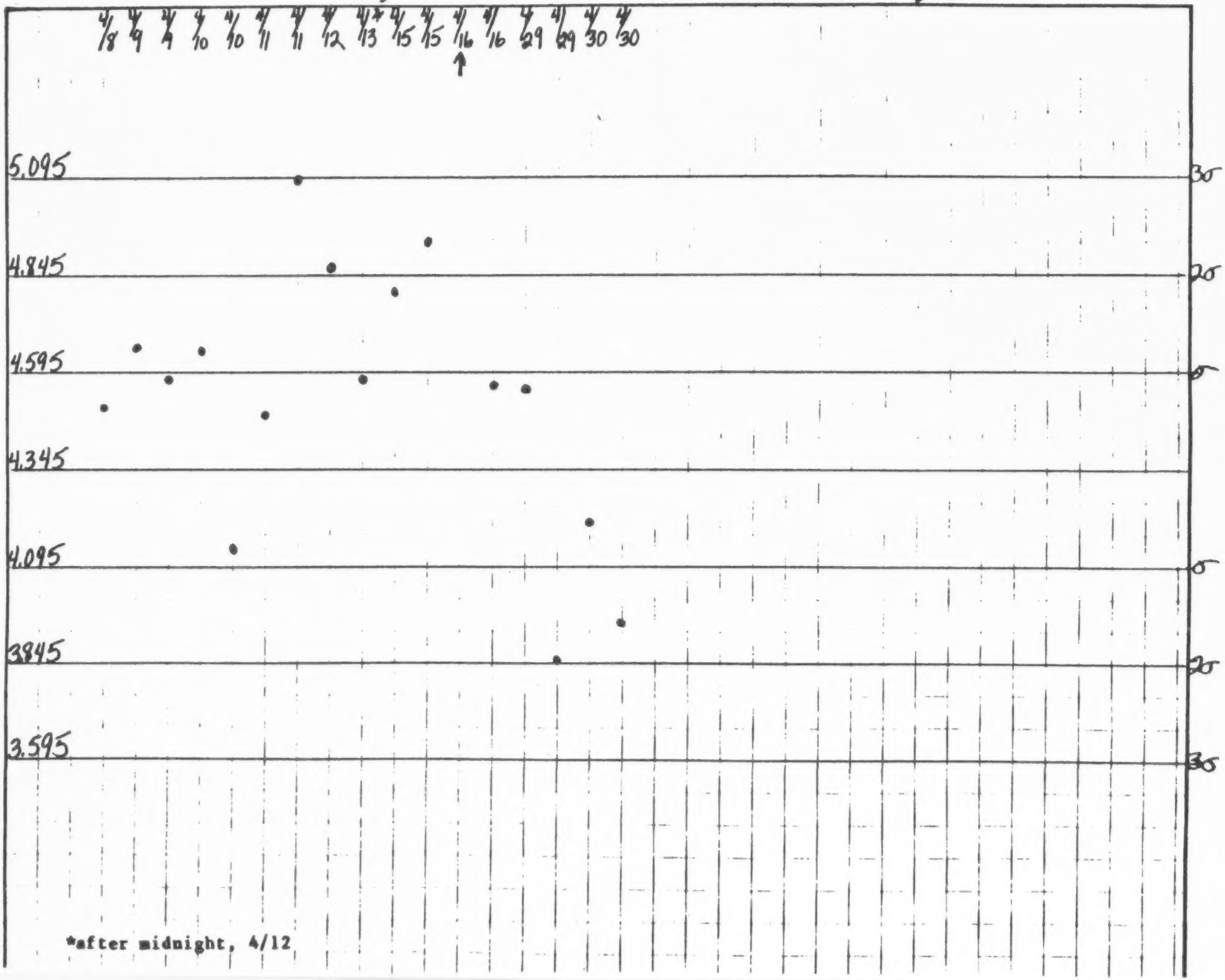
(Example for d_8-Chlorobenzene)

Response Factor Control Chart (d_8-chlorobenzene, mass 54)



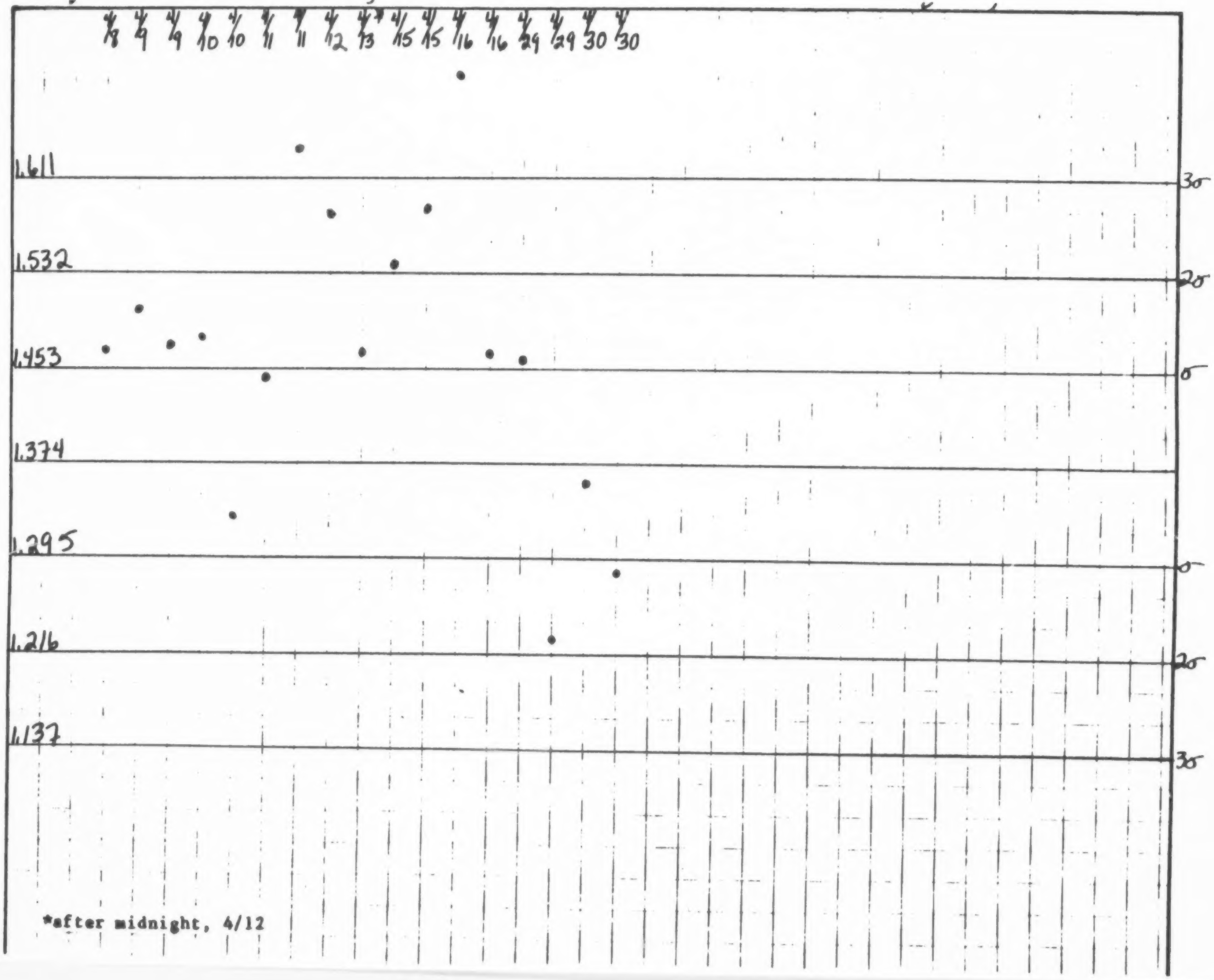
*after midnight, 4/12

Response Factor Control Chart (d_5-chlorobenzene, mass 117)



*after midnight, 4/12

Response Factor Control Chart (d_5-chlorobenzene, mass 119)



*after midnight, 4/12

DAILY TUNING DATA

(Examples)

RADIAN
CORPORATION

GC/MS PERFORMANCE STANDARD

Decafluorotriphenylphosphine

INSTRUMENT ID 5100 DATE 4/1/85 TIME 15:17

FRN 5AAA 262 QC REPORT NO. 1 ANALYST RP

TUNE CHECK:

m/e	Ion Abundance Criteria	% Relative Abundance
51	30 - 60% of mass 198	50.4
68	less than 2% of mass 69	— ( )1
69	mass 69 relative abundance	52.4
70	less than 2% of mass 69	— ( )1
127	40 - 60% of mass 198	44.5
197	less than 1% of mass 198	—
198	base peak, 100% relative abundance	100.0
199	5 - 9% of mass 198	6.4
275	10 - 30% of mass 198	17.3
365	greater than 1% of mass 198	1.1
441	less than mass 443	7.6
442	greater than 40% of mass 198	57.2
443	17 - 23% of mass 442	10.5 (18.4)2

1Value in parenthesis is % mass 69.
2Value in parenthesis is % mass 442.

Comments:

QC Form 8409

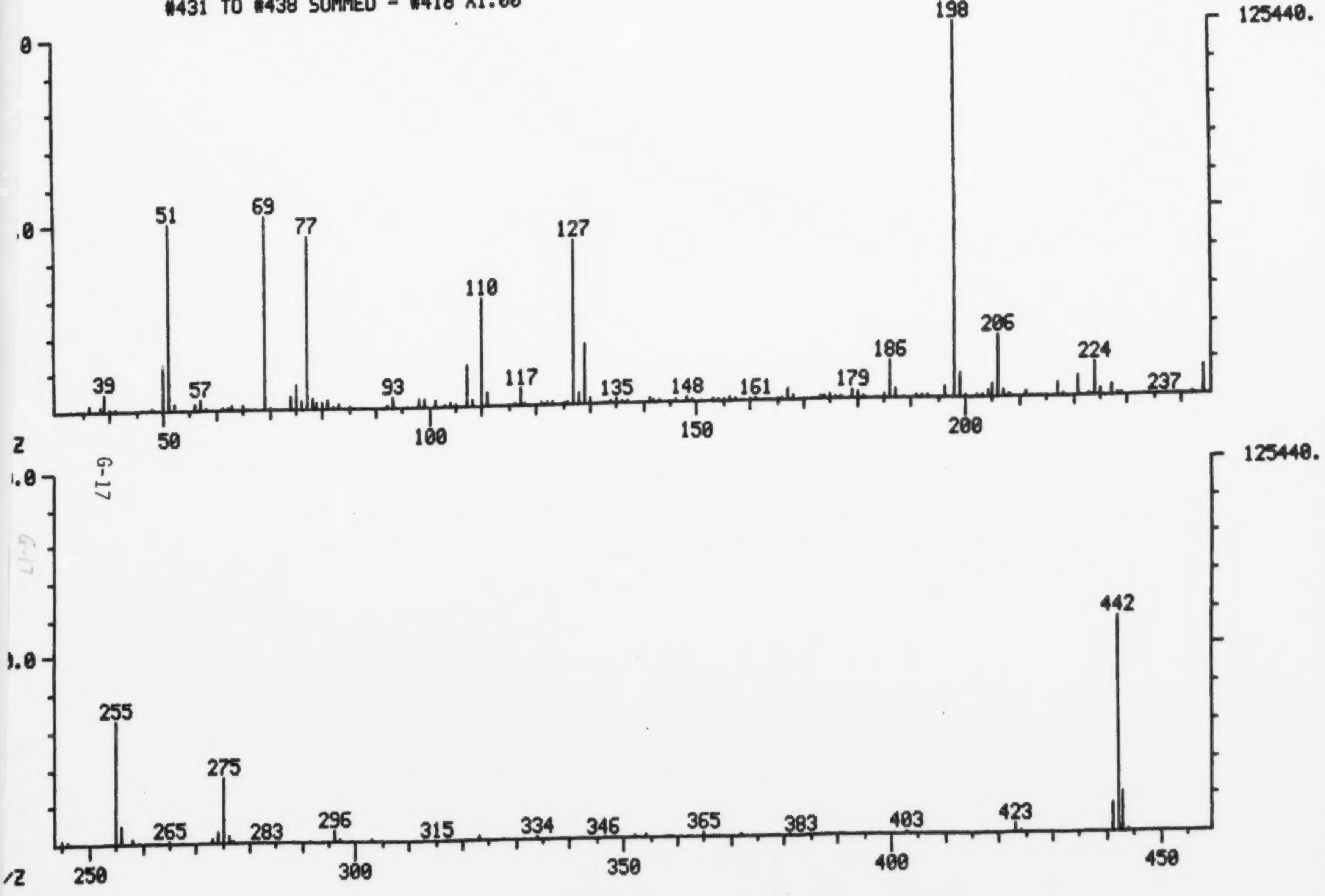
Project No. ______

Book No. ______ TITLE SAAA262 DFTPP 50ng

MASS SPECTRUM
04/01/85 15:17:00 + 7:14
SAMPLE: DFTPP 50 NG
CONDS.: EI
GC TEMP: 257 DEG. C
#431 TO #438 SUMMED - #418 X1.00

DATA: SAAA262
CALI: 5AAA262 #2

RIC: 886784.



```
Mass List                                  Data: 5AAA262 # 434        Base m/z:   198
04/01/85 15:17:00 +  7:14                  Cali: 5AAA262 #   2        RIC:     886784.
Sample: DFTPP 50 NG
Conds.: EI
 #431 to #438 Summed - #418 X1.00

      36          0.00     0.00          0. Minima       Min inten:     658.
     445                                 #  0 Maxima
    Mass          % RA    % RIC       Inten.         Mass            % RA    % RIC      Inten.

   36.00?  S      2.09     0.30        2620.       161.00    S       0.90     0.13       1124.
   38.00?  S      1.43     0.20        1790.       167.00            3.22     0.46       4036.
   39.00?  S      4.50     0.64        5640.       168.00            1.26     0.18       1578.
   50.00?  S     12.47     1.76       15648.       174.00    S       0.59     0.08        736.
   51.00?  S     50.41     7.13       63232.       175.00            1.20     0.17       1502.
   52.00?  S      2.06     0.29        2580.       176.00            0.78     0.11        974.
   56.00?  S      1.52     0.21        1904.       177.00            0.70     0.10        881.
   57.00?  S      2.82     0.40        3536.       179.00            2.24     0.32       2812.
   61.00?         0.56     0.08         706.       180.00            1.60     0.23       2004.
   63.00?  S      1.31     0.19        1644.       181.00            0.73     0.10        911.
   65.00?  S      1.07     0.15        1344.       185.00    S       1.05     0.15       1322.
   69.00   S     52.35     7.40       65664.       186.00           10.01     1.42      12560.
   74.00   S      3.56     0.50        4464.       187.00    S       2.61     0.37       3272.
   75.00   S      6.63     0.94        8320.       192.00            0.68     0.10        854.
   76.00          2.26     0.32        2832.       193.00            0.78     0.11        980.
   77.00   S     46.68     6.60       58560.       196.00            2.83     0.40       3544.
   78.00   S      3.08     0.44        3864.       198.00          100.00    14.15     125440.
   79.00   S      2.04     0.29        2564.       199.00            6.44     0.91       8080.
   80.00          2.01     0.28        2524.       204.00            1.97     0.28       2476.
   81.00   S      2.47     0.35        3104.       205.00            3.64     0.52       4568.
   82.00   S      0.71     0.10         892.       206.00           16.91     2.39      21216.
   83.00   S      1.14     0.16        1436.       207.00    S       1.96     0.28       2456.
   85.00   S      0.77     0.11         968.       211.00            0.97     0.14       1220.
   92.00   S      0.61     0.09         764.       217.00            3.55     0.50       4448.
   93.00   S      3.02     0.43        3792.       221.00    S       5.48     0.77       6872.
   98.00   S      2.31     0.33        2892.       223.00            0.77     0.11        967.
   99.00          2.34     0.33        2940.       224.00            8.81     1.25      11056.
  101.00          1.65     0.23        2076.       225.00            2.08     0.29       2604.
  104.00          0.93     0.13        1172.       227.00            2.76     0.39       3468.
  105.00   S      0.68     0.10         852.       229.00            0.53     0.07        665.
  107.00   S     11.33     1.60       14208.       244.00            7.66     1.09       9632.
  108.00          1.82     0.26        2284.       245.00            1.15     0.16       1446.
  110.00   S     29.08     4.11       36480.       255.00           32.86     4.65      41216.
  111.00   S      3.88     0.55        4864.       256.00            4.92     0.70       6176.
  117.00   S      4.83     0.68        6064.       258.00            1.19     0.17       1492.
  121.00          0.57     0.08         720.       273.00            0.96     0.14       1202.
  123.00   S      0.76     0.11         956.       274.00            3.11     0.44       3896.
  125.00          0.62     0.09         779.       275.00           17.30     2.45      21696.
  127.00   S     44.49     6.29       55808.       276.00            2.00     0.28       2508.
  128.00   S      3.00     0.42        3760.       277.00            0.85     0.12       1060.
  129.00   S     16.45     2.33       20640.       296.00            2.93     0.41       3680.
  130.00   S      1.73     0.24        2172.       323.00            1.32     0.19       1660.
  135.00   S      1.32     0.19        1656.       334.00            0.65     0.09        812.
  137.00   S      0.65     0.09         818.       365.00            1.09     0.15       1368.
  141.00          1.43     0.20        1796.       372.00            0.58     0.08        732.
  142.00          0.62     0.09         775.       423.00            2.51     0.35       3144.
  148.00          1.48     0.21        1852.       441.00            7.60     1.08       9536.
  153.00          0.55     0.08         690.       442.00           57.24     8.10      71808.
  155.00          0.82     0.12        1026.       443.00           10.48     1.48      13152.
  156.00          1.45     0.21        1824.       444.00            0.81     0.11       1019.
```

No.__

essed & Understood by me.   Date   Date

RADIAN
CORPORATION

GC/MS PERFORMANCE STANDARD

Decafluorotriphenylphosphine

INSTRUMENT ID 5100 DATE 4/2/85 TIME 9:06

FRN 5AAA 265 QC REPORT NO. 2 ANALYST RP

TUNE CHECK:

m/e	Ion Abundance Criteria	% Relative Abundance	
51	30 - 60% of mass 198	57.7	
68	less than 2% of mass 69	1.5	(2.5)[1]
69	mass 69 relative abundance	60.6	
70	less than 2% of mass 69	—	( )[1]
127	40 - 60% of mass 198	47.5	
197	less than 1% of mass 198	—	
198	base peak, 100% relative abundance	100.0	
199	5 - 9% of mass 198	6.9	
275	10 - 30% of mass 198	16.2	
365	greater than 1% of mass 198	1.02	
441	less than mass 443	8.2	
442	greater than 40% of mass 198	63.3	
443	17 - 23% of mass 442	11.4	(18.0)[2]

[1] Value in parenthesis is % mass 69.
[2] Value in parenthesis is % mass 442.

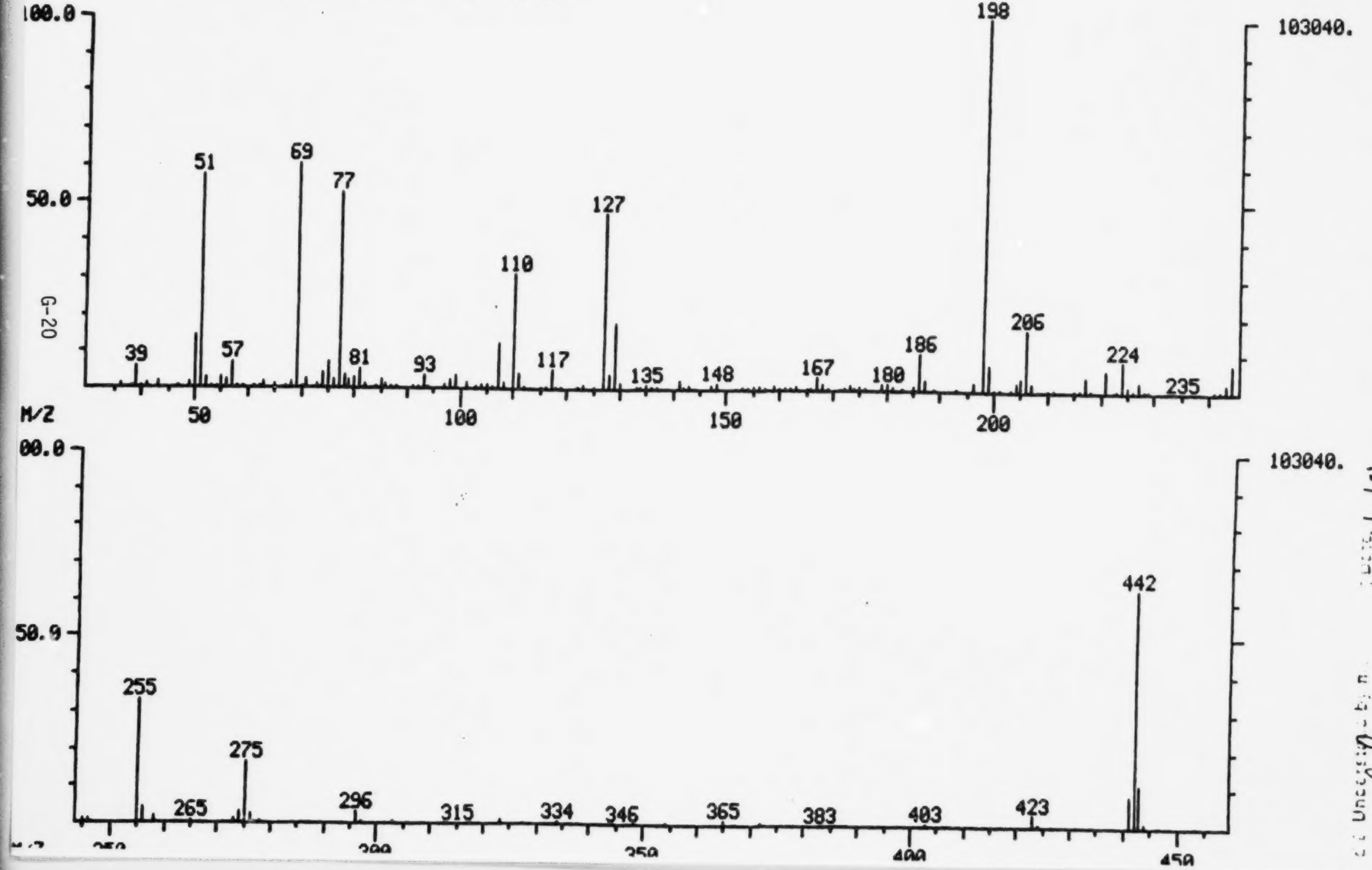
Comments:

6

MID MASS SPECTRUM
04/02/85 9:06:00 + 7:11
SAMPLE: DFTPP
CONDS.: EI
GC TEMP: 256 DEG. C
#442 TO #445 SUMMED - #457 X1.00

DATA: 5AAA265 #443
CALI: 5AAA264 #2

BASE M/Z: 198
RIC: 824320.



8/1/8

```
MID Mass List                         Data: 5AAA265 # 443        Base m/z:   198
04/02/85  9:06:00 +  7:11             Cali: 5AAA264 #   2        RIC:     824320.
Sample: DFTPP
Conds.: EI
 #442 to #445 Summed - #457 X1.00

    35          0.00    0.00       0.  Minima      Min inten:     896.
   445                             #   0  Maxima
  Mass          % RA   % RIC    Inten.          Mass        % RA   % RIC    Inten.

   36.00?  S    1.16    0.15     1198.        148.00   S    1.71    0.21     1764.
   39.00?  S    5.82    0.73     6000.        155.00   S    0.98    0.12     1012.
   41.00?  S    1.30    0.16     1340.        156.00   S    1.46    0.18     1500.
   43.00?  S    2.05    0.26     2108.        159.00   S    1.36    0.17     1400.
   49.00?  S    1.58    0.20     1628.        161.00   S    0.88    0.11      908.
   50.00?  S   14.47    1.81    14912.        163.00   S    0.96    0.12      988.
   51.00?  S   57.70    7.21    59456.        165.00   S    0.87    0.11      896.
   52.00?  S    2.99    0.37     3084.        167.00   S    3.75    0.47     3864.
   53.00?  S    0.89    0.11      912.        168.00   S    2.07    0.26     2132.
   55.00?  S    3.04    0.38     3132.        173.00   S    1.45    0.18     1492.
   56.00?  S    2.22    0.28     2288.        174.00   S    0.89    0.11      920.
   57.00?  S    7.42    0.93     7648.        175.00   S    1.10    0.14     1132.
   63.00?  S    1.92    0.24     1976.        179.00   S    1.55    0.19     1592.
   65.00?  S    1.09    0.14     1120.        180.00   S    1.72    0.21     1768.
   68.00?  S    1.50    0.19     1544.        181.00   S    1.12    0.14     1152.
   69.00   S   60.62    7.58    62464.        185.00   S    1.24    0.16     1280.
   71.00   S    2.53    0.32     2608.        186.00   S   10.30    1.29    10608.
   73.00   S    1.32    0.16     1356.        187.00   S    3.06    0.38     3156.
   74.00   S    3.96    0.49     4076.        196.00   S    2.52    0.31     2596.
   75.00   S    7.45    0.93     7680.        198.00   S  100.00   12.50   103040.
   76.00   S    2.58    0.32     2660.        199.00   S    6.92    0.86     7128.
   77.00   S   52.55    6.57    54144.        204.00   S    2.19    0.27     2256.
   78.00   S    3.35    0.42     3452.        205.00   S    3.64    0.45     3748.
   79.00   S    2.39    0.30     2464.        206.00   S   17.05    2.13    17568.
   80.00   S    2.81    0.35     2892.        207.00   S    2.11    0.26     2172.
   81.00   S    5.31    0.66     5472.        217.00   S    3.95    0.49     4072.
   82.00   S    1.16    0.15     1200.        221.00   S    5.75    0.72     5920.
   85.00   S    2.34    0.29     2416.        224.00   S    8.66    1.08     8928.
   86.00   S    1.35    0.17     1390.        225.00   S    2.03    0.25     2088.
   93.00   S    3.59    0.45     3696.        227.00   S    2.79    0.35     2876.
   97.00   S    1.09    0.14     1118.        229.00   S    0.88    0.11      904.
   98.00   S    2.36    0.30     2436.        243.00   S    2.48    0.31     2560.
   99.00   S    3.63    0.45     3740.        244.00   S    7.86    0.98     8104.
  101.00   S    1.71    0.21     1766.        245.00   S    1.37    0.17     1416.
  104.00   S    0.93    0.12      962.        246.00   S    1.13    0.14     1164.
  105.00   S    1.23    0.15     1264.        255.00       33.17    4.15    34176.
  107.00   S   12.59    1.57    12976.        256.00   S    4.19    0.52     4320.
  108.00   S    1.66    0.21     1712.        258.00   S    1.89    0.24     1944.
  110.00   S   30.93    3.87    31872.        273.00        0.97    0.12      999.
  111.00   S    4.49    0.56     4624.        274.00   S    2.92    0.36     3008.
  117.00   S    5.28    0.66     5440.        275.00   S   16.21    2.03    16704.
  123.00   S    1.04    0.13     1072.        276.00   S    2.17    0.27     2232.
  127.00   S   47.52    5.94    48960.        296.00        2.96    0.37     3048.
  128.00   S    4.29    0.54     4424.        323.00        1.25    0.16     1292.
  129.00   S   18.07    2.26    18624.        365.00        1.02    0.13     1046.
  130.00   S    1.60    0.20     1648.        423.00        3.15    0.39     3244.
  135.00   S    0.91    0.11      936.        441.00        8.21    1.03     8464.
  141.00   S    2.20    0.28     2272.        442.00   S   63.29    7.91    65216.
  143.00   S    1.40    0.18     1444.        443.00       11.38    1.42    11728.
                                              444.00        0.96    0.12      994.
```

RADIAN
CORPORATION

GC/MS PERFORMANCE STANDARD

Decafluorotriphenylphosphine

INSTRUMENT ID 5100 DATE 4/3/85 TIME 10:21
FRN 5AAA273 QC REPORT NO. 3 ANALYST RP

TUNE CHECK:

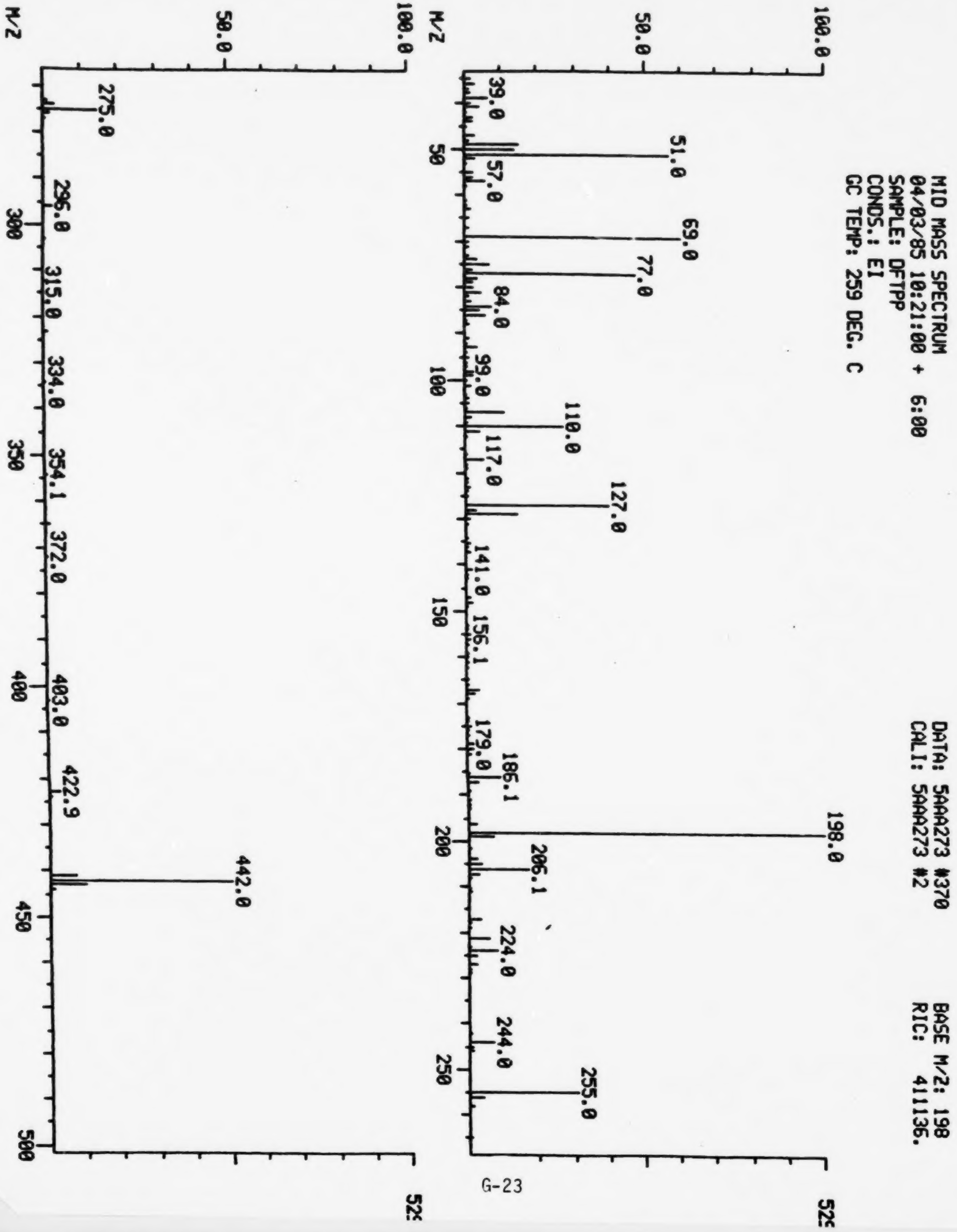
m/e	Ion Abundance Criteria	% Relative Abundance	
51	30 - 60% of mass 198	57.1	
68	less than 2% of mass 69	—	( )[1]
69	mass 69 relative abundance	60.5	
70	less than 2% of mass 69	0.9	(1.5)[1]
127	40 - 60% of mass 198	40.2	
197	less than 1% of mass 198	—	
198	base peak, 100% relative abundance	100.0	
199	5 - 9% of mass 198	6.7	
275	10 - 30% of mass 198	14.6	
365	greater than 1% of mass 198	1.1	
441	less than mass 443	6.7	
442	greater than 40% of mass 198	49.9	
443	17 - 23% of mass 442	10.1	(20.2)[2]

[1] Value in parenthesis is % mass 69.
[2] Value in parenthesis is % mass 442.

Comments:

Project No. ______

Book No. ______ TITLE SAAA273 DFTPP 50ng



MID MASS SPECTRUM
04/03/85 10:21:00 + 6:00
SAMPLE: DFTPP
CONDS.: EI
GC TEMP: 259 DEG. C

DATA: SAAA273 #370
CALI: SAAA273 #2

BASE M/Z: 198
RIC: 411136.

```
MID Mass List                        Data: 5AAA273 # 370         Base m/z:   198
04/03/85 10:21:00 +  6:00            Cali: 5AAA273 #   2         RIC:     411136.
Sample: DFTPP
Conds.: EI

   35          0.00     0.00         0.  Minima      Min inten:       463.
  444                                #   0  Maxima
  Mass         % RA    % RIC     Inten.            Mass          % RA   % RIC      Inten.

  35.01?F      1.74     0.22       921.          117.02 F        5.04    0.65      2672.
  36.03?F      2.66     0.34      1410.          123.08 F        1.04    0.13       550.
  36.96?       0.93     0.12       495.          127.04 F       40.16    5.18     21280.
  38.04?F      1.83     0.24       971.          128.03 F        2.95    0.38      1564.
  39.05?F      6.27     0.81      3320.          129.02 F       14.60    1.88      7736.
  40.02?F      1.56     0.20       827.          130.05          1.05    0.14       558.
  41.07?F      4.10     0.53      2172.          135.06          1.36    0.17       719.
  43.08?F      2.57     0.33      1360.          137.14 F        0.93    0.12       494.
  44.02?F      2.47     0.32      1310.          141.02          1.45    0.19       771.
  47.02?       3.01     0.39      1594.          147.06 F        1.09    0.14       580.
  48.01?F      1.30     0.17       691.          148.02          1.51    0.19       798.
  49.01?F     15.14     1.95      8024.          155.05          0.89    0.11       470.
  50.05?F     13.74     1.77      7280.          156.06          1.44    0.19       765.
  51.04?F     57.13     7.36     30272.          167.08 F        3.45    0.44      1826.
  52.04?F      2.67     0.34      1416.          168.02 F        2.14    0.28      1136.
  55.05?F      2.22     0.29      1174.          175.09          1.17    0.15       621.
  56.04?F      2.16     0.28      1146.          179.03 F        1.99    0.26      1056.
  57.04?F      5.98     0.77      3168.          180.03 F        1.47    0.19       780.
  63.02?       1.91     0.25      1012.          181.06          0.88    0.11       468.
  65.05?       1.22     0.16       646.          186.06 F        9.53    1.23      5048.
  67.05?F      0.97     0.12       512.          187.05 F        2.68    0.34      1418.
  68.96 F     60.51     7.80     32064.          196.11 F        2.59    0.33      1374.
  70.07 F      0.93     0.12       492.          198.00 F      100.00   12.89     52992.
  71.07        1.18     0.15       627.          199.00 F        6.70    0.86      3548.
  73.09 F      0.92     0.12       490.          204.05          2.15    0.28      1138.
  74.03 F      3.54     0.46      1878.          205.05 F        3.55    0.46      1882.
  75.03 F      6.79     0.87      3596.          206.06 F       16.91    2.18      8960.
  76.06 F      2.26     0.29      1200.          207.06 F        3.01    0.39      1594.
  77.05 F     47.71     6.15     25280.          216.98 F        3.23    0.42      1714.
  78.07 F      3.22     0.42      1708.          221.14 F        6.05    0.78      3204.
  79.03 F      2.16     0.28      1146.          224.05 F        8.02    1.03      4248.
  80.03 F      2.08     0.27      1104.          225.05 F        2.26    0.29      1198.
  81.05 F      4.43     0.57      2348.          226.94          2.57    0.33      1362.
  82.04 F      1.29     0.17       682.          244.05 F        7.08    0.91      3752.
  83.04 F      2.03     0.26      1076.          245.05          0.89    0.12       474.
  83.98 F      7.79     1.00      4128.          246.03 F        0.96    0.12       508.
  85.03 F      3.93     0.51      2084.          255.02 F       30.56    3.94     16192.
  85.97 F      5.78     0.75      3064.          256.00 F        4.15    0.54      2200.
  88.01        1.01     0.13       535.          258.00 F        1.30    0.17       690.
  91.04 F      0.89     0.12       473.          273.00          0.92    0.12       487.
  93.02 F      3.70     0.48      1960.          274.03 F        2.75    0.35      1458.
  95.12 F      1.02     0.13       543.          275.03 F       14.64    1.89      7760.
  98.04 F      2.17     0.28      1150.          276.03 F        1.92    0.25      1020.
  99.02 F      2.51     0.32      1328.          296.00          2.40    0.31      1274.
 101.02        1.62     0.21       859.          323.06          1.11    0.14       587.
 104.03 F      0.92     0.12       489.          364.97          1.10    0.14       584.
 105.03 F      1.01     0.13       536.          422.91 F        2.84    0.37      1506.
 107.03 F     11.11     1.43      5888.          441.00 F        6.73    0.87      3564.
 108.03        1.64     0.21       871.          442.00 F       49.88    6.43     26432.
 110.03 F     27.05     3.49     14336.          443.00 F       10.14    1.31      5376.
 111.05        4.02     0.52      2128           444.00 F        0.93    0.12       495.
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RADIAN
CORPORATION

GC/MS PERFORMANCE STANDARD

Decafluorotriphenylphosphine

INSTRUMENT ID 5100 DATE 4/4/85 TIME 9:03
FRN 5AAA277 QC REPORT NO. 4 ANALYST RP

TUNE CHECK:

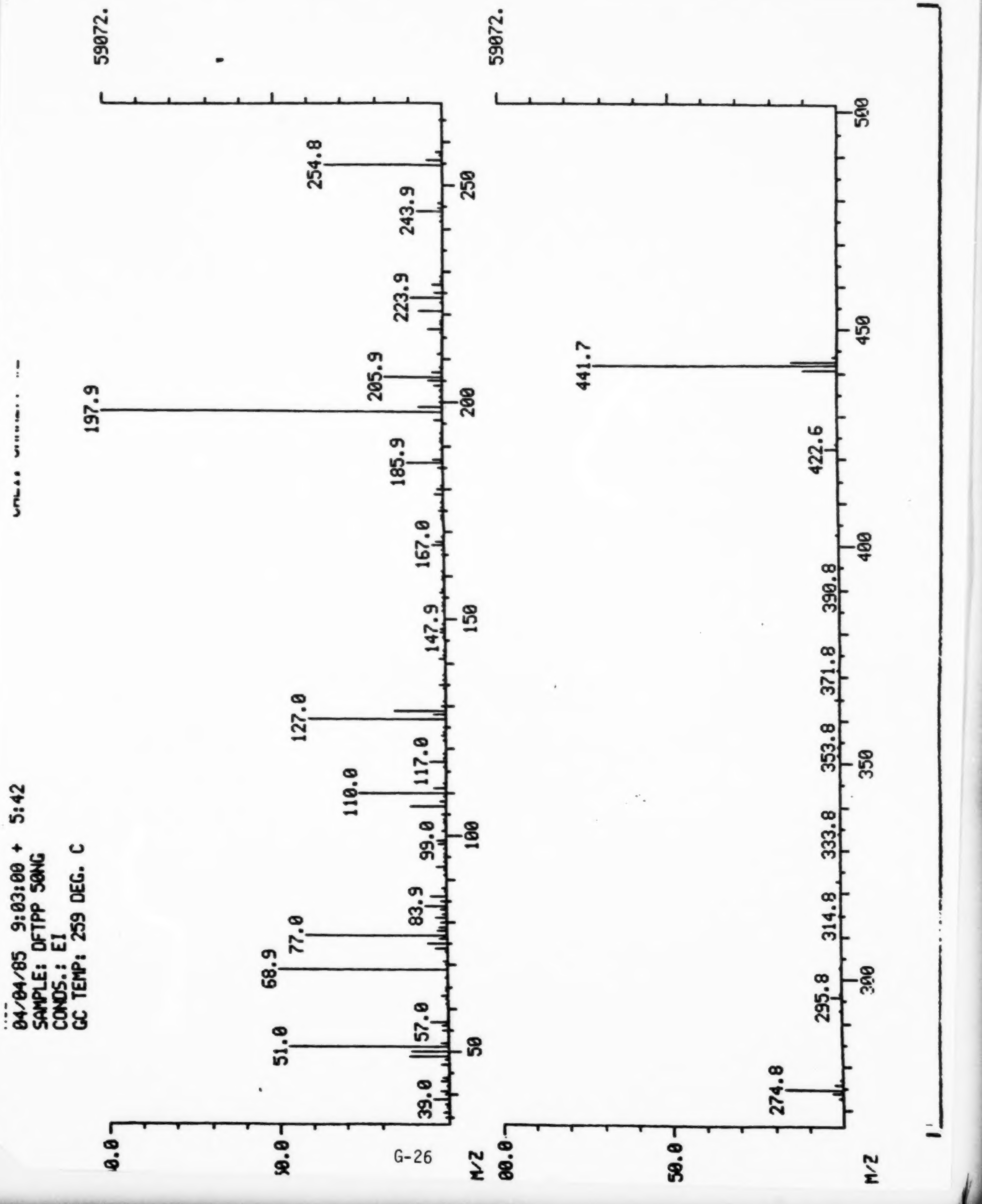
m/e	Ion Abundance Criteria	% Relative Abundance
51	30 - 60% of mass 198	47.3
68	less than 2% of mass 69	— ( )[1]
69	mass 69 relative abundance	50.0
70	less than 2% of mass 69	0.8 (1.6)[1]
127	40 - 60% of mass 198	40.5
197	less than 1% of mass 198	—
198	base peak, 100% relative abundance	100.0
199	5 - 9% of mass 198	6.8
275	10 - 30% of mass 198	17.0
365	greater than 1% of mass 198	1.3
441	less than mass 443	9.6
442	greater than 40% of mass 198	71.5
443	17 - 23% of mass 442	13.3 (18.6)[2]

[1] Value in parenthesis is % mass 69.
[2] Value in parenthesis is % mass 442.

Comments:

Project No. ________

Book No. _______ TITLE 5AAA277



04/04/85 9:03:00 + 5:42
SAMPLE: DFTPP 50NG
CONDS.: EI
GC TEMP: 259 DEG. C

```
MID Mass List                         Data:  5AAA277 # 352        Base m/z:   198
04/04/85  9:03:00 +  5:42             Cali:  5AAA277 #   2        RIC:      451584.
Sample:  DFTPP 50NG
Conds.:  EI

   35          0.00     0.00           0.  Minima     Min inten:     467.
  444                               #   0  Maxima
  Mass         % RA    % RIC     Inten.         Mass          % RA   % RIC      Inten.

  35.00?       1.38     0.18       817.       129.92          1.16    0.15        684.
  35.98?       1.95     0.25      1150.       134.97          1.52    0.20        897.
  38.01?F      1.06     0.14       628.       137.02 F        0.81    0.11        480.
  39.02?F      4.60     0.60      2716.       140.94 F        1.50    0.20        889.
  39.98?F      1.16     0.15       685.       146.94          0.97    0.13        575.
  41.02?F      2.36     0.31      1392.       147.91          1.42    0.19        841.
  43.06?F      2.13     0.28      1260.       154.92          0.82    0.11        482.
  43.98?F      1.71     0.22      1012.       155.95 F        1.39    0.18        824.
  46.97?       2.07     0.27      1222.       160.94          0.82    0.11        483.
  48.01?F      1.08     0.14       639.       166.95 F        3.35    0.44       1978.
  48.98?F     11.82     1.55      6984.       167.94 F        2.14    0.28       1266.
  50.01?F     10.89     1.42      6432.       174.95 F        1.17    0.15        692.
  51.02?F     47.29     6.19     27936.       178.89 F        2.36    0.31       1394.
  52.02?       2.29     0.30      1350.       179.91 F        1.64    0.21        969.
  55.06?F      1.66     0.22       982.       180.94          0.84    0.11        498.
  56.00?F      1.86     0.24      1098.       184.92          1.09    0.14        643.
  57.01?F      5.17     0.68      3056.       185.94 F       10.37    1.36       6128.
  63.00?F      1.64     0.21       967.       186.92 F        2.64    0.35       1562.
  65.02?       0.87     0.11       514.       195.95 F        2.59    0.34       1528.
  68.92 F     50.00     6.54     29536.       197.86 F      100.00   13.08      59072.
  70.02 F      0.83     0.11       489.       198.87 F        6.84    0.89       4040.
  71.05        1.00     0.13       589.       203.91 F        2.10    0.28       1242.
  74.01 F      3.39     0.44      2004.       204.92 F        3.99    0.52       2356.
  74.97 F      5.89     0.77      3480.       205.92 F       16.87    2.21       9968.
  76.04 F      2.11     0.28      1248.       206.92          3.05    0.40       1802.
  77.01 F     41.60     5.44     24576.       210.95 F        0.95    0.12        562.
  78.02 F      2.95     0.39      1744.       216.84 F        3.91    0.51       2308.
  78.98 F      2.32     0.30      1372.       220.98 F        6.81    0.89       4020.
  79.96 F      1.96     0.26      1156.       222.83 F        0.84    0.11        498.
  80.97 F      3.26     0.43      1924.       223.89 F        9.03    1.18       5336.
  81.99 F      1.12     0.15       661.       224.89 F        2.22    0.29       1312.
  83.03 F      1.52     0.20       897.       226.80          2.87    0.38       1694.
  83.92 F      6.52     0.85      3852.       243.87 F        7.71    1.01       4552.
  84.99 F      1.51     0.20       894.       244.91 F        1.07    0.14        632.
  85.92 F      4.49     0.59      2652.       245.84          0.89    0.12        525.
  87.93 F      1.04     0.14       613.       254.84 F       34.62    4.53      20448.
  90.97        0.85     0.11       504.       255.84 F        4.74    0.62       2800.
  92.95 F      3.18     0.42      1880.       257.81 F        1.47    0.19        866.
  97.96 F      2.23     0.29      1320.       272.84 F        0.88    0.11        519.
  98.97 F      2.76     0.36      1632.       273.84 F        3.01    0.39       1780.
 100.97        1.22     0.16       720.       274.84 F       16.96    2.22      10016.
 104.98        1.00     0.13       592.       275.84 F        2.15    0.28       1270.
 106.97 F     10.22     1.34      6040.       276.81 F        0.86    0.11        509.
 107.98 F      1.71     0.22      1012.       295.78          3.12    0.41       1846.
 109.96 F     25.54     3.34     15088.       322.81          1.31    0.17        773.
 110.98 F      3.49     0.46      2060.       364.72 F        1.27    0.17        749.
 116.95 F      4.77     0.62      2820.       422.62 F        3.45    0.45       2036.
 122.98        0.97     0.13       572.       440.69 F        9.62    1.26       5680.
 126.95 F     40.52     5.30     23936.       441.69 F       71.51    9.35      42240.
 127.95 F      3.21     0.42      1898.       442.72 F       13.26    1.73       7832.
 128.92 F     15.36     2.01      9072.       443.72 F        1.07    0.14        633.
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itnessed & Understood by